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Analytical Capabilities of Complex Formations in Functional Organic Analysis

927M0236A Moscow ZHURNAL ANALITICHESKOY KHMII in Russian Vol 47 No 6, Jun 92 (manuscript received 16 Apr 91) pp 994-1002

[Article by S. I. Obtemperanskaya, Moscow State University; UDC 543.8]

[Abstract] This is one of a series of papers presented at the All Union Conference on Analytical Chemistry of Organic Compounds held in Moscow, 23-25 June 1991. In a review type article the author covered the following topics: functional analysis of a mixture of organic compounds as complexes with charge transfer or ion-radicals; functional analysis of organic compounds in form of σ -complexes, and metal complexes in functional organic analysis. A multitude of complexes can be used in such an analysis: coordination compounds, molecular complexes, σ -complexes, ion-radical salts, ion pairs, etc. The actual analytical determination is carried out by means of spectrometry, potentiometric titrimetry, fluorimetry, various types of chromatographic separations, etc. This is a lecture type presentation without obvious original data being reported; most of the citations came from the work of the author: 21 out of 25 Russian citations. Table 1; references 33: 25 Russian, 8 Western.

Volt-Amperometry With Ultra-Microelectrodes - New Step of Method Development

927M0236B Moscow ZHURNAL ANALITICHESKOY KHMII in Russian Vol 47 No 6, Jun 92 (manuscript received 7 May 91) pp 1003-1013

[Article by V. N. Maystrenko, I. A. Rusakov, G. K. Budnikov, Bashkir State University, Ufa; Kazan State University; UDC 543.253]

[Abstract] This is one of a series of papers presented at the All Union Conference on Analytical Chemistry of Organic Compounds held in Moscow, 23-25 June 1991. The goal of this review was to familiarize the analysts with basic principles of the electro-chemical methods of analysis and to present current advances and directions in which they could be applied in volt-amperometry. No such reviews have appeared in Russian literature thus far. The paper covers three aspects: the design of ultra microelectrodes, characteristics of volt-amperometry with ultra-microelectrodes and application of ultra-microelectrodes to the in vivo experiments, analysis of polymers and non-conducting solid phases, in microanalyses, etc. References 94: 3 Russian, 91 Western.

Some Analytical Problems in Petroleum Chemistry

927M0236C Moscow ZHURNAL ANALITICHESKOY KHMII in Russian Vol 47 No 6, Jun 92 (manuscript received 21 Feb 91) pp 1033-1040

[Article by S. L. Davydova, N. V. Rastova, Institute of Petrochemical Synthesis imeni A. V. Topchiyev, Russian Academy of Sciences, Moscow UDC 543:541.49: 665.7.033]

[Abstract] This is one of a series of papers presented at the All Union Conference on Analytical Chemistry of Organic Compounds held in Moscow, 23-25 June 1991. Because the use of oil is constantly increasing, the role of heavy petroleum residues, asphaltenes, tars, coke, etc. is also increasing. The use of such products necessitates accurate determination of the composition of all components, including heavy metals (V, Ni, Fe, Cu, Mn, Co, Zn, etc.). Methods for the preparation of test samples for atomic adsorption spectroscopy, UV spectrophotometry and EPR using the ion selective electrodes are being constantly improved. For determination of V, Ni and other metals, a recommendation was made to use the flame technique of atomic adsorption spectrometry. To determine the degree of oxidation, the EPR method was used effectively. However, individual specimens may require specific solutions; therefore a variety of modern analytical methods and instrumentations is needed for accurate determination of the composition of metal containing petroleum products. Tables 5; figures 2; references 17: 13 Russian, 4 Western.

Multielement Analysis of Osmium- and Ruthenium-Organic Compounds

927M0236G Moscow ZHURNAL ANALITICHESKOY KHMII in Russian Vol 47 No 6, Jun 92 (manuscript received 9 Mar 92) pp 1118-1122

[Article by I. G. Barakovskaya, N. E. Gelman, Ya. A. Terentyeva, A. G. Buyanovskaya, Institute of Metal-Organic Compounds imeni A. N. Nesmeyanov, Russian Academy of Sciences, Moscow; UDC 543.8]

[Abstract] This is one of a series of papers presented at the All Union Conference on Analytical Chemistry of Organic Compounds held in Moscow, 23-25 June 1991. In this paper development of a multielement analysis of organic compounds was reported; the test samples could include rare metals such as Os and Ru, or F, I, Si, S, B and others. Many such compounds belong to the clusters class which are of theoretical interest. An earlier reported gravimetric method of analysis was optimized expanding the range of its application to multiple compositions and more complex structures. It was possible to determine four elements from one sample (C, H, Os, F) by adding spectrophotometry to the gravimetric procedure. The standard deviations for C, H, and Os were 0.17, 0.08 and 0.35 respectively. Table 1; figure 1; references: 8 (Russian).

Some Cost Calculating Methods for Analytical Work

927M0236H Moscow ZHURNAL ANALITICHESKOY KHMII in Russian Vol 47 No 6, Jun 92 (manuscript received 6 May 91) pp 1140-1142

[Article by I. A. Iliyeva, Moscow Scientific Production Association "Syntez", Moscow; UDC 338.512: 543.001.24]

[Abstract] This is one of a series of papers presented at the All Union Conference on Analytical Chemistry of Organic Compounds held in Moscow, 23-25 June 1991. Transition of many organizations and businesses to self-sufficiency and independent budgeting made it mandatory to expand their economic concepts. Market effect, free pricing, increasing competition raise the issue of how to save analytical laboratories, how to increase their scientific and technical capabilities and how to safeguard their economic basis. The cost of analytical "product" can be calculated on the basis of three components: 1) ready,

routine methodology, 2) chemical analysis of materials based on available "generic" methods and 3) development of new methods. Some statistical data (governmental estimates) were reported on cost of chromatographic determinations, cost of expensive, advanced technology equipment use in rubles per hours of operation, and cost of routine analyses. Obviously all these estimates are only orientational in nature because as soon as they appeared, the prices went up several-fold due to inflation. Transfer to a full market economy will produce further refinements. Tables 3; references: 3 (Russian).

Catalytic Dehydrogenation and Dehydrooligomerization of Cycloalkanes Under Effect of Rhenium and Tertiary Phosphine Complexes

927M0179A Moscow NEFTEKHIMIYA in Russian Vol 32 No 2, Mar-Apr 92 (manuscript received 18 Aug 91) pp 99-105

[Article by Ye. I. Bagriy and A. B. Amerik, Institute of Petrochemical Synthesis imeni Topchiyeva, RAN; UDC 542.971:541.128:546.82:547.512:547.592.3]

[Abstract] A study of synthesized metaloorganic complexes of the $L_1L_2Re(PMe_3)_2$ type in reaction of dehydrogenation of cycloalkanes at 80-100°C and use of tertiary-butylethylene as a hydrogen acceptor showed that, upon addition to such complexes of triethylaluminum into reaction products, there was formed, together with cycloolefins, their dimers and trimers, that is, reaction of cycloalkanes dehydrogenation was accompanied by oligomerization of the forming cycloalkanes. The concentration of cyclooctene became constant after reaction of 90 minutes but the oligomers yield continued to increase. The study indicated the fundamental possibility of creating metallocatalysts of activation of alkanes of polyfunctional action. References 18: 6 Russian, 12 Western.

Effect of Reaction Medium on Characteristics of Nickel-containing Oxide Catalyst for Thermal Oxidation Cracking of Mazut

927M0179B Moscow NEFTEKHIMIYA in Russian Vol 32 No 2 Mar-Apr 92 (manuscript received 13 Nov 91) pp 125-129

[Article by R. B. Akhverdiyev, L. M. Mirzayeva, A. D. Guseynova et al., Institute of Petrochemical Processes imeni Yu. G. Mamedaliyev, Baku, Institute of Organic Chemistry imeni N. D. Zelinskiy, RAN Moscow; UDC 541.128]

[Abstract] A study of the effect of the reaction medium on the physico-chemical characteristics of a new nickel-containing oxide catalyst of thermal oxidative treatment of mazut, produced on the base of a Ni-Al-alloy, promoted In and Ga. Cracking the mazut produced oxidation-reduction processes with occurrence of transitions of $NiAl_2O_4$ and NiO into Ni^0 . Recrystallization of highly dispersed Al particles, present in the initial catalyst, occurred. There was a strong tendency of Ni and Al particles to be localized. Gasification of the coked catalyst produced reduction of NiO and In_2 to Ni^0 and In_2O_3 . Some part of the NiO and In_2O_3 phases became amorphous. Regeneration of the catalyst in each cycle restored the physico-chemical characteristics of the sample. Figures 2; references 5 (Russian).

Kinetic Regularities of Reaction of Catalytic Alkylation of Phenol by Methanol

927M0179C Moscow NEFTEKHIMIYA in Russian, Vol 32 No 2 Mar-Apr 92 (manuscript received 9 Aug 90) pp 141-147

[Article by A. A. Agayev, D. B. Tagiyev and A. Z. Tagiyev, Azerbaijan Institute of Petroleum and Chemistry imeni M. Azizbekov, Baku; UDC 541.127.001.572:66.095.253.7+547.561.1]

[Abstract] A study of the mechanism and kinetic regularities of alkylation of phenol by methanol on zeolite catalyst type Y and compilation of a kinetic model of the method of producing a mixture of o- and n-cresols was described and discussed. The proposed mathematical model of the kinetics of the heterogenic-catalytic process of alkylation of phenol by methyl alcohol satisfactorily described regularities of the reaction in the recommended temperature range $T=603-643$ K volume velocity for liquid raw material $0.25-1.0$ hr⁻¹ and molar ratio of phenol:methanol of (2-1):(1-2). The yield of o- and n-cresols on the reacting phenol was 74-94.6 percent. Figure 1; references 10: 7 Russian; 3 Western.

Catalytic Hydroxylation of Benzoic Acid by Hydrogen Peroxide

927M0179D Moscow NEFTEKHIMIYA in Russian Vol 32 No 2, Mar-Apr 92 (manuscript received 15 Nov 91) pp 159-161

[Article by E. A. Karakhanov, Ch. Retish Pulippurasseril, T. Yu. Filippova et al.; Moscow State University imeni M. V. Lomonosov; UDC 547.532.943.7]

[Abstract] Results of catalytic hydroxylation of benzoic acid by hydrogen peroxide were presented and discussed. An effective catalytic system based on Fe(III) and surfactants for hydroxylation of benzoic acid by hydrogen peroxide in an aqueous medium at 30-80°C was proposed. The basic product of the reaction was salicylic acid, the selectivity of formation of which exceeded 70 percent under the best conditions. Catalysts based on Fe(III) were most active. Addition of polyethers to the catalytic system increased benzoic acid conversion. Figures 8 (Western).

The Reactivity of Red and Orange Allotropic Modifications of Wilkinson's Complex as a Catalyst for the Hydroformylation of Allyl Alcohol

927M0181D Moscow KOORDINATSIONNAYA KHIMIYA in Russian Vol 18 No 6, May 92 (manuscript received 23 Oct 91) pp 636-641

[Article by G.A. Korneyeva, M.P. Filatova, R.V. Chekhova, V.G. Avakyan, M.M. Potarin, Ye.V. Slivinskiy, and S.M. Loktev, Petrochemical Synthesis Institute imeni A.V. Topchiyev, Russian Academy of Sciences; UDC 547.361]

[Abstract] A comparison was made of the catalytic and spectral properties of solutions of red and orange allotropic modifications of Wilkinson's complex as a catalyst for the hydroformylation of allyl alcohol. The hydroformylation of allyl alcohol was conducted in a 0.25-l steel autoclave under a constant gas pressure of 1 MPa (an equimolar synthesis gas composition was used) at 70° in toluene. The reaction rate was controlled by the rate at which the gas was absorbed from the high-pressure feed tank. The allyl alcohol was fed into the reactor with the catalytic solution. The red modification of Wilkinson's complex was synthesized as published elsewhere at the boiling point of ethanol (78°), and the orange modification was produced analogously but at temperatures not exceeding 70°. A Specord M-80 spectrophotometer was used to record IR spectra, a Specord M-40 spectrophotometer was used to record ESR spectra, and an MSL-300 Bruker spectrometer operating under anaerobic conditions at 25° and atmospheric pressure was used to record NMR spectra. Both the red and orange versions of Wilkinson's complex resulted in the formation of *trans*-[RhCl(S)(PPh₃)₂] when reacted with CO in organic solvents and synthesis gas as described above. The spectral characteristics of the *trans*-[RhCl(S)(PPh₃)₂] were demonstrated to depend on the modification of Wilkinson's complex used. Preliminary studies of the kinetics of the hydroformylation of allyl alcohol in the presence of both modifications of Wilkinson's complex used as the precursor of a catalyst established that the reaction proceeds about five times faster when the red modification is used. The orange modification is metastable and is quantitatively transformed into the red modification at temperatures above 78-80°. The spectral studies performed established significant differences between the red and orange modifications that were evidently linked to their structural peculiarities. Specifically, distortions in the plane-quadratic structure of Wilkinson's complex were discovered. The greater structural distortion found in the case of the red modification was deemed likely to be the result of a reaction of the rhodium atom with the hydrogen atom located in the *o*-position of the triphenylphosphine's benzene ring. The catalytic system produced from the red modification of Wilkinson's complex was found to manifest higher activity in the hydroformylation of allyl alcohol at the above conditions than did the catalytic system formed from the orange modification. No difference in the selectivities of the two hydroformylation catalysts or in their formation of reaction by-products were recorded. Figures 2, table 1; references 7: 2 Russian, 1 Western.

Synthesis of Onium Polyoxometallates of Mo and W and Photoinduced Oxidation of Hydrocarbons Under Conditions of Interface Catalysis

927M0182A Moscow NEFTEKHIMIYA in Russian
Vol 32 No 1, Jan-Feb 92 (manuscript received
18 Apr 91) pp 12-17

[Article by Ye.N. Karaulova, Ye.I. Bagriy, A.I. Mikaya, and L.R. Barykina, Petrochemical Synthesis Institute

imeni A.V. Topchiev, USSR Academy of Sciences, Moscow; UDC 547.279.2:912.551.2.541.145.542.943.546.215]

[Abstract] New sulfonium and ammonium polyoxometallates of tungsten and molybdenum were synthesized. The gross formulas and yields of the newly synthesized compounds were as follows: C₃₀H₃₉Mo₁₂O₄₃PS₃ (86.0%), C₃₃H₄₅Mo₁₂O₄₃PS₃ (92.5%), C₃₀H₃₉Mo₁₂O₄₆PS₃ (76.0%), C₃₃H₄₅Mo₁₂O₄₃PS₃ (90%), C₃₃H₄₅O₄₃PS₃W₁₂ (91.7%), C₃₀H₃₉O₄₆PS₃W₁₂ (77.0%), C₄₅H₅₄Mo₁₂N₃O₄₃PS₃ (91.0%), and C₈₄H₁₅₂N₄O₃₂W₁₀ (51.6%). The new onium polyoxometallates were then studied from the standpoint of their use as catalysts of the oxidation of hydrocarbons under conditions of interface catalysis. C₈₄H₁₅₂N₄O₃₂W₁₀ was then used to catalyze the photoinduced oxidation of cyclohexane and adamantane. The interface catalysis was conducted at a process temperature of 80°C for 2 hours. In the case of cyclohexane, 0.11 mole of the hydrocarbon was added to 0.0048 mole H₂O₂ and 1.96 x 10⁵ moles C₈₄H₁₅₂N₄O₃₂W₁₀ (for a catalyst:oxidizing agent:substrate ratio of 1:245:5,812) and a yield of 9 moles of oxidation products per mole catalyst. The composition of the reaction products was as follows (%): cyclohexanol + cyclohexanone, ≤8; dicyclohexyl (with a cyclohexylcyclohexene impurity), 31; dicyclohexyl ether, 36; dicyclohexyl peroxide, 12; and unidentified oxidation products, 13. In the case of adamantane, 0.01 mole was combined with 0.01 mole H₂O₂ and 3.92 moles C₈₄H₁₅₂N₄O₃₂W₁₀ (for a catalyst:oxidizing agent:substrate ratio of 1:255:255) and a yield of 12.5 moles of oxidation products per mole catalyst. The composition of the reaction products was as follows (%): adamantanol-1, 38.6; and adamantanol-2, 61.4 (with a 20% adamantanone impurity). Tables 2; references 18: 6 Russian, 12 Western.

Hydrogenation of Benzene on a Nickel Catalyst Produced by Sputtering in Argon Plasma

927M0182B Moscow NEFTEKHIMIYA in Russian
Vol 32 No 1, Jan-Feb 92 (manuscript received
30 Nov 90) pp 18-24

[Article by S.I. Serdyukov, M.S. Safonov, P.S. Chumak, O.I. Veselkova, V.K. Belnov, I.V. Nizhnikova, and A.A. Fomin, Moscow State University imeni M.V. Lomonosov; UDC 542.941.7.547.532:546.74]

[Abstract] An investigation was made of the catalytic properties of a planar catalyst produced by sputtering nickel onto a nickel substrate. The catalyst was studied from the standpoint of its behavior in a benzene hydrogenation reaction. The catalyst was prepared by sputtering PNK-2K-10 nickel onto nickel foil 0.2 mm thick. The foil had first been subjected to fine-stream treatment. Fractions of nickel powder with dispersions of 30-40, 40-70, and 70-100 μm were used to prepare the planar catalyst. The thickness of the catalytic coating was determined by the duration of sputtering and varied from 60 to 525 μm. A Dron-2 x-ray diffractometer (Cu-α radiation) was used to conduct an x-ray phase analysis of

the sputtered coatings, and a JAMP-10 was used to perform scanner Auger electron spectroscopy studies on the specimens. The hydrogenation of benzene was conducted under a pressure of 0.1 MPa at temperatures of 393 to 513 K by placing 0.05 to 0.3 g catalyst in a heated quartz microreactor. The hydrogen used in the reaction was produced by decomposing intermetallide hydrides based on La-Ni. The oxygen impurity content did not exceed $10^{-3}\%$ (vol). A Khrom-5 chromatograph was used to perform a quantitative analysis of the hydrocarbon mixture at the reactor's outlet. The hydrogenation reaction products were analyzed every 4 to 6 minutes on an LKhM-8MD chromatograph; the area of the chromatographic peaks was determined by using an ITs-26 interpreter. The x-ray phase analysis studies established that the study catalytic coating is indeed crystalline nickel. The Auger electron spectroscopy analysis established that Ni, C, and O are all present in the specimen's composition and that both the carbon and oxygen contents decrease significantly as the depth of the layer increases. The catalytic coating's structure was quite nonuniform and macroporous. The specific surface of the applied nickel layer turned out to be practically equal to the specific surface of the starting powder, i.e., $0.1 \text{ m}^2/\text{g}$ for powder with a dispersion of 30 to 50 μm . The planar nickel catalyst produced was demonstrated to be over an order of magnitude more active than the starting nickel powder under the benzene hydrogenation pressure and temperatures studied. Cyclohexane was the only benzene transformation product detected. The planar catalyst did not require pretreatment in a hydrogen atmosphere and became active immediately after vapors of C_6H_6 in an H_2 stream were fed into the reactor. The latter fact was taken as evidence that the surface nickel oxide is reduced by the reaction mixture at temperatures up to 513 K. The new catalyst's activity stabilized in 1 hour or less and remained constant for a long time thereafter. The new nickel catalyst did not lose its activity after storage at room temperature in air. Heat treatment in an H_2 stream did result in deactivation of the catalytic coating, however. Figures 3, table 1; references 7: 5 Russian, 2 Western.

Photometric Oxidation of Hydrocarbons by Air in Solutions Catalyzed by the Complex AuCl_4^-

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25 Feb 91) pp 37-42

[Article by G.V. Nizova and G.B. Shulpin, Chemical Physics Institute imeni N.N. Semenov, USSR Academy of Sciences, Moscow; UDC 541.127]

[Abstract] The authors of the study reported herein examined the photochemical oxidation of hydrocarbons catalyzed by the ion AuCl_4^- in the aprotic organic solvents CH_3CN and CH_2Cl_2 . All of the reactions were conducted in air in cylindrical glass vessels (diameter, 20 mm) equipped with water-cooled sleeves. The reactions were all conducted under conditions of intensive stirring by magnetic stirrers. Ten milliliters of reaction solutions

was used. The oxidation product yields were determined by gas-liquid chromatography on an LKhM-80/6 chromatograph with the sorbent Inerton AW-HMDS 315-320 μm impregnated with 5% Carbowax 1,500. Argon was used as the carrier gas. The reaction temperature ranged from 50 to 170° with a heating rate of 4°/min. A Philips PU 8700 spectrophotometer was used to record the absorption spectra. The main reaction products of the photochemical oxidation (by light with a wavelength of $\lambda > 310 \text{ nm}$) of cyclohexane by an NaAuCl_4 complex in a CH_3CN solution in relatively high concentration ($1.5 \times 10^{-2} \text{ M}$) were chlorocyclohexane and cyclohexane (that was identified in the form 1,2-dibromocyclohexane after bromine had been added). Reducing the concentration of AuCl_4^- in the CH_3CN when the cyclohexane solution was irradiated with light ($\lambda > 310 \text{ nm}$) in air resulted in a situation where the main reaction products were cyclohexanol and cyclohexanone in quantities significantly greater than the amount of complex used. No chlorocyclohexane was detected in the reaction product mixture when the AuCl_4^- concentration equaled $5 \times 10^{-4} \text{ M}$. Both oxygenation products were initially accumulated at a high rate. After about 1 hour, the accumulated rate began to decline (especially in the case of cyclohexanol). Only 3 hours after the beginning of the irradiation was an increase in the rate of oxygenation product accumulation observed. This latter accumulation rate subsequently remained constant. The reaction was determined to occur via several routes involving the participation of chloride ligands and the formation of catalytically active peroxide gold complexes. Figures 3, table 1; references 24: 18 Russian, 6 Western.

Zeolite Promoters of Al-Ni-Mo Catalysts of Thiophene Desulfurization

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27 Apr 90) pp 49-57

[Article by A.V. Vysotskiy, G.D. Chukin, Bratsk Industrial Institute, Bratsk, and All-Union Oil Refining Scientific Research Institute, Moscow; UDC 542.97.3: 541.128.13:661.183.6:665.656]

[Abstract] Na forms of first-generation zeolites (types Y and M) along with high-silica, borosilicate [BSZ], ferrosilicate [FSZ], aluminosilicate [ASZ] (types TsVK, TsVN, and TsVM), and ultrahigh-silica zeolites [UHSZ] were examined. Their primary objective in so doing was to select active promoters of the hydrodesulfurization of thiophene on reduced Al-Ni-Mo [ANM] catalysts. The zeolite-containing Al-Ni-Mo catalysts were prepared by adding 5 to 10% (mass) zeolite to a pseudo-boehmite-type suspension of aluminum hydroxide. The resultant mass was dried in air at 120°C for 3 hours and roasted at 550°C for 5 hours. Molybdenum and nickel were added by the impregnation method, after which the catalysts were sulfurized by thiophene. The pulse method was used to estimate catalytic activity. Each catalyst was activated in a hydrogen stream at 400°C for 1 hour. The study specimens were also subjected to gas

chromatography analysis on an LKhM-8 MD chromatograph. The studies performed indicated that the various promoters studied manifested different degrees of effectiveness in different processes. As far as activity in hydrogenolysis, the catalysts rank as follows: UHSZ > BSZ > NaM > TsVK > ANM. As hydrogenation promoters, the zeolites rank as follows: UHSZ > BSZ > TsVK > ANM > NaM. Finally, as cracking promoters, the study zeolites may be ranked as follows: TsVK > ANM > BSZ > NaM > UHSZ. In order to predict the catalytic activity of zeolite-promoters and select active additive-modifiers for Al-Ni-Mo hydrodesulfurization catalysts, the researchers examined the dependence of specimens' activity on the silicate modulus of the zeolite. The optimal catalytic functions were observed when the zeolite-promoters had silicate moduli of 5-10, 60-90, and 200-1,100. The optimal Na₂O content for zeolite-promoters was found to be 1 to 2% (mass). The researchers also presented a scheme for transforming thiophene on a reduced zeolite-promoted Al-Ni-Mo catalyst. Figures 4, table 1; references 18: 17 Russian, 1 Western.

New Catalytic Systems for Hydrocarbon Oxidation and Cracking Processes

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[Article by M.I. Levinbuk and V.B. Melnikov, Grozno Scientific Research Institute and GANIG imeni I.M. Gubkin [not further identified]; UDC 66.097.3]

[Abstract] One way of developing the catalytic transformations of hydrocarbons is to expand the thresholds of their thermodynamic limits without significantly altering process parameters. This would make it possible to increase yields on existing equipment and to also develop new processes. Combining carbonium-ion transformations and redox reactions of hydrocarbons in a single catalytic process would make it possible to significantly expand the thermodynamic limits of hydrocarbon conversion. In view of these facts, the authors of the study reported herein examined new catalytic systems for hydrocarbon oxidation and cracking processes. A reagent catalyst was compared with the commercial catalysts Durabed-12 (Mobil Oil) and Tseokar-3f3 (USSR). The reagent catalyst contained the following (mass percent): SiO₂, 78.96; Al₂O₃, 7.5; Na₂O, 0.22; rare earth elements, 1.50; Fe₂O₃, 0.10; and Me_nO_m, 11.5. The new reagent catalyst was more selective with respect to the formation of benzene with a higher octane number. This increased selectivity was attributed to a change in the chemical composition of the benzene fraction. The catalysts Tseokar-3f3 and Durabed-12 have benzene fractions with chemical compositions that are very similar to one another (and hence octane numbers that are very close to one another), even though the matrix of Durabed-12 contains α-Al₂O₃. The benzene fraction produced on the reagent catalyst, on the other hand, contains fewer paraffins while containing similar

amounts of naphthenes and aromatics. The higher octane numbers of the benzene fraction of the reagent catalyst are attributed to the fact that the new catalyst contains monoolefins and an increased amount of diene hydrocarbons (which also explains the new catalyst's high iodine number). The authors also concluded that the appearance of oxygen-containing compounds in the benzene fraction and higher content of products of complete hydrocarbon oxidation would seem to indicate that the oxygen of the variable-valence metal oxide of the reagent catalyst is involved in the process of the cracking of vacuum gas oil that was studied. Table 1; references 4: 1 Russian, 3 Western.

Oxidation of Hydrogen Sulfide from Coke Oven Gas over New Catalysts, Including Activated Charcoal

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[Article by V. G. Lipovich, M. A. Kapustin, Ye. V. Dombrovskiy, S.A. Kolomin, and V. T. Popov, High Temperatures Institute; UDC 541.128:662.642]

[Abstract] Coke oven gas is normally purged of hydrogen sulfide and other sulfur compounds by adsorption methods in conjunction with ethanol amine, cold methanol, arsenic salts, and ammonia solutions. The hydrogen sulfide is desorbed in the next stage, then oxidized to sulfur dioxide and sulfur trioxide or sulfuric acid or isolated as elemental sulfur. These methods decrease the hydrogen sulfide content in the off gases by one or two orders of magnitude. One disadvantage is the low efficiency of the process making it necessary to use large scale equipment with high capital investment. In the present work a study was made of hydrogen sulfide conversion over catalysts containing transition metals and activated charcoal. Chromium-containing catalysts were demonstrated to be the most active. References 1 (Russian).

The Catalytic Activity of Secondary Aromatic Amines in the Reaction of a 2,4,6-Tri-tert-butylphenoxy Radical With a Hydrocarbon and the Reactivity of Aminyl Radicals in the Reaction of Separation of an H Atom From Cumene

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[Article by V.T. Varlamov, Chemical Physics Institute, USSR Academy of Sciences, Chernogolovka; UDC 541.128.12:541.127:547.534.1:547.63+547.563.024]

[Abstract] This study examined nine substituted diphenylamines as potential catalysts of the reaction of 2,4,6-tri-tert-butyl phenoxy [ArO[•]] with cumene. The studies performed established that secondary aromatic amines

(4,4'-substituted diphenylamines [AmH]) catalyze the reaction of an ArO^\bullet with cumene. The catalysis is caused by the partial replacement of ArO^\bullet by aminyl radicals $[\text{Am}^\bullet]$ (in a quasi-equilibrium reaction of ArO^\bullet with AmH with an equilibrium constant of K_3), which have proved to be much more active in separating H from RH (rate constant, k_4) than ArO^\bullet is. The catalysis rate constant (i.e., $k_{\text{cat}} = K_3 k_4$) was found for eight of the substituted diphenylamines at 370 K. The catalytic activity of AmH was found to increase as the electron-donor nature of the substituents increased: $\lg k_{\text{cat}}^{370} = -(3.9 \pm 0.6) \text{ to } -(1.16 \pm 0.13) \sigma^+$. The value of k_4 , on the other hand, was found to increase as the electron-acceptor nature of the substituents increased: $\lg k_4^{370} = -(0.438 \pm 0.086) + (0.52 \pm 0.19) \sigma$. A linear dependence of $\lg k_4$ on the thermal effect of the reaction was discovered: $\lg k_4^{370} = -(1.98 \pm 0.48) + (0.046 \pm 0.015) q$. The author concludes by stating that a quantitative study of the catalytic activity of AmH in the reaction of ArO^\bullet with cumene may be used as a method of determining the absolute values of k_4 . The values of k_4 found for AmH (VI) in the study reported herein are said to be in good agreement with published results obtained by the method of kinetic spectrophotometry of the products of the reaction $\text{Am}^\bullet + \text{RO}_2$ during the thermal decomposition of tetraphenylhydrazine in O_2 -saturated ethylbenzene. The author acknowledges that the values of k_4 reported herein are not highly precise; however, he goes on to state that their precision may be increased somewhat by comparing several values found for k_4 with one another. Figures 3, table 1; references 16: 15 Russian, 1 Western.

The Kinetics and Mechanism of the Catalyzed Oxidation of Polybutadiene by Molecular Oxygen

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[Article by A.V. Nikitin, S.N. Kholuyskaya, and V.L. Rubaylo, Chemical Physics Institute imeni N.N. Semanova, USSR Academy of Sciences, Moscow; UDC 542.943.7:541.124.2:[546.21+547.315]:541.64]

[Abstract] Kinetics and mechanism of the catalytic oxidation of oligomeric cis-polybutadiene ($M \approx 1,500$) by molecular oxygen in the presence of complex Cu (II), Ni (II), and V (IV) compounds were examined. The study reactions were conducted at 50° in ethylbenzene. The acceptor 1,2-bis-(4,4'-dimethylaminophenyl)-1,2-dipthaloylthane was used to make a quantitative determination of the rate at which radicals were generated. The structure of the oxidized polybutadiene was studied by Fourier IR spectroscopy. The studies performed established that in the presence of a copper complex, the oxidation process is of the nature of a free-radical chain process and that the copper chelate participates in the stage of degenerate branching. The studies further revealed that the chelate Ni (II) catalyzes the oxidation of polybutadiene in accordance with a molecular or latent-radical mechanism, whereas the

complex $\text{VO}(\text{DMSO})_5(\text{ClO}_4)_2$ acts in accordance with a molecular mechanism. The Fourier IR spectroscopy studies established that the reaction product formed in the presence of the Cu (II) chelate is identical to the product of the initiated oxidation of polybutadiene. The presence of Ni (II) was found to result in the formation of a polymer containing only -OOH groups in the α -position of the C=C bond. No more than one hydroperoxide group per link was found. A set of oxygen-containing products and a decrease in the number of C=C bonds was discovered in the presence of the complex $\text{VO}(\text{DMSO})_5(\text{ClO}_4)_2$. Unlike in the case of low-molecular olefins (cyclohexene), the oxidation of polybutadiene in the presence of V (IV) was found to entail the destruction of the C=C bond of the oligomer chain. Figures 2; references 11: 8 Russian, 3 Western.

Kinetics of the Isomerization of Dichlorobutenes Catalyzed by Iron (III) Chloride

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[Article by V.V. Smirnov, Ye.N. Golubeva, and T.N. Rostovshchikova, Chemistry Department, Moscow State University imeni M.V. Lomonosov; UDC 541.128.3:541.124-145.4:542.952.1:547.413.15]

[Abstract] The kinetics of the isomerization of 3,4-dichlorobutene-1 into 1,4-dichlorobutene-2 catalyzed by iron (III) chloride in a medium of organochlorine solvents was examined. The solvents and reagents were purified by the standard methods. The amount of water in the system was determined by measuring the volume of hydrogen evolved during a reaction with lithiumaluminumhydride. All of the operations were performed in an inert atmosphere. The concentration of iron chloride in the solution was determined by using potassium rhodanide as described elsewhere and by spectrophotometry based on absorption in the near-UV range. The concentration of dichlorobutenes in the reaction mixture was determined by gas-liquid chromatography on Chrom-5 and Tsvet chromatographs. The proton magnetic resonance method was used to perform a series of control experiments. The experiments performed established that the isomerization of 3,4-dichlorobutene-1 into 1,4-dichlorobutene-2 catalyzed as described is characterized by unusual kinetic laws: a high variable catalyst order and inhibition of the reaction by dichlorobutene. Specifically, the kinetic curves of the isomerization of 3,4-D into 1,4-D in a medium of chloroform and methylene chloride with a constant concentration of catalyst linearizes in coordinates corresponding to a first-order reversible reaction, i.e., $d[1,4\text{-D}]/dt = k_1^{\text{eff}}[3,4\text{-D}] - k_2^{\text{eff}}[1,4\text{-D}]$, where the values of the effective constants k_1^{eff} and k_2^{eff} depend on the concentration of catalyst and the total concentration of dichlorobutenes $[1,4\text{-D} + 3,4\text{-D}]$. The effective isomerization rate constants found at 295 K are 1-2 orders of magnitude higher than those found by Gulnev in his 1987 dissertation for hexahydro iron (III) chloride in the absence of a solvent at a

temperature of 370. The effective reaction order with respect to the catalyst at the concentration studied (1.5 M) remained equal to 4 throughout the entire range of temperatures studied. The observed activation energy of the forward reaction was 57 ± 14 kJ/mol, while that of the reverse reaction was 71 ± 16 kJ/mol. Under the conditions studied (i.e., a [3,4-D]₀ concentration of 1.5 M, an [FeCl₃]₀ concentration of 0.001 M, and a reaction temperature of 295 K), varying the dielectric constant of the solvent in the interval from 6 to 9 was found to have virtually no effect on the effective rate constant. When the researchers analyzed their results with consideration for the state of the iron (III) chloride in the solution, they found two factors to be key: First, the iron chloride in weakly polar media exists in the form of the dimer Fe₂Cl₆. Second, the inhibition of the reaction by an excess of substrate points to the formation of a catalytically inactive complex between the substrate and catalyst. As alternatives to previously published hypotheses regarding the mechanism of the isomerization of dichlorobutenes by iron (III) chloride, the authors propose a mechanism with intermediate transfer of an electron from the chlorolefin to the iron chloride oligomer or a synchronous mechanism with displacement of the chlorine in the transition complex containing two molecules of dimeric iron (III) chloride and dichlorobutene. Figures 3, table 1; references 7: 5 Russian, 2 Western.

The Micellar-Catalytic Oxidation of Hydrocarbons. III. The Kinetics and Mechanism of the Oxidation of Cumene by Oxygen in Aqueous Solutions of Sodium Dodecylsulfate in the Presence of Copper Sulfate

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[Article by L.P. Panicheva, N.Yu. Tretyakov, and A.Ya. Yuffa, Tyumen State University; UDC 542.943.7:541.124.7-145.2: 546.562'226:547.535:54-148]

[Abstract] A mechanism of chain oxidation of cumene by oxygen in aqueous solutions of sodium dodecylsulfate in the presence of copper sulfate was proposed. According to the proposed mechanism (which is based on an analysis of a set of experimental data), initiation of the chains occurs on the surface of the drops of emulsion and in the straight micelles of the surfactant, where oil-soluble reagents and water-soluble catalysts can concentrate, while the growth and quadratic breaking of the chains occurs in the hydrocarbon phase. The question of how the resultant radicals pass from the micelles and into the drops of emulsion is left open; it is hypothesized to occur either in a process of diffusion through the aqueous phase or when the micelles collide with the drops of emulsion. After the reaction has been completed, the emulsion is stratified into a hydrocarbon phase (containing unoxidized cumene and hydrogen peroxide) and an aqueous phase (containing the surfactant and catalyst [Cu²⁺]). The catalyst-containing micellar aqueous phase is demonstrated to retain its

activity even after repeated use. An equation is provided that is said to result in a satisfactory description of the dependence of the oxidation rate on the hydrocarbon concentration and the initiation rate when a phenomenological approach to the problem is taken. Micellar metal complex catalysts are thus shown to be superior to homogeneous catalysts in that they make it easier to separate the catalyst from the reaction product and to regenerate the catalyst after use. Figures 4, table 1; references 8: 5 Russian, 3 Western.

Kinetics and Mechanism of the Heterogeneous Catalytic Epoxydation of Olefins. II. Epoxydation of Styrene in the Presence of Molybdenum Selenide and Cyclohexene in the Presence of Tungsten Selenide

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[Article by T.V. Filippova, S.V. Timofeyev, A.L. Smirnova, and E.A. Blyumberg, Chemical Physics Institute imeni N.N. Semenov, USSR Academy of Sciences, Moscow; UDC 541.128.3:542.943.7'95:541.124: [546.772'23+547.535.024-39+547.538.141]

[Abstract] The kinetic laws and composition of the products of the reaction of cumyl hydroperoxide with styrene catalyzed by molybdenum selenide and cyclohexenyl hydroperoxide with cyclohexene in the presence of tungsten selenide were studied. The epoxydation of styrene by cumyl hydroperoxide was conducted in a sparger-type reactor equipped with a magnetic stirrer and reflux condenser in an argon current at 70 and 90°. The concentration of cumyl hydroperoxide in the styrene was varied from 0.1 to 0.5 mol/l. The styrene epoxydation rate was kept unchanged within the bounds of the measurement error (10 to 20%) while the mixer rotation speed was increased by a factor of 1.8 (thus confirming that the reaction was occurring the kinetic region). The purification of the styrene and chromatographic analysis of the reaction products were conducted as described elsewhere. The epoxydation experiments were performed at a temperature of 70° in accordance with a previously published procedure. Several of the soluble compounds (o-chloranyl, anthracene, di(tert-butylphenyl)nitroxyl) used to modify the catalyst were introduced directly into the liquid phase. The method of treating the catalyst with drops of liquid followed by drying and loading into the reactor before the start of the heating process was used in the case of anthracene. The oxygen modification was conducted by placing the catalyst into an empty reactor, evacuating it and then filling it with oxygen, and then removing the oxygen and conducting the reaction in an argon atmosphere. The autocatalytic nature of the kinetic curves plotted for the formation of styrene oxide and dimethylphenylcarbinol and the consumption of the cumene hydroperoxide in the epoxydation of styrene by cumene hydroperoxide in the presence of MoSe₂ led the researchers to hypothesize

that just as is the case during the epoxidation of cyclohexene, the catalyst is activated during the course of the process. The reaction rate was found to increase fivefold as the degree of conversion with respect to cumene hydroperoxide increased (from 10 to 20%) and to then decrease on account of the consumption of the cumene hydroperoxide. No slowing of the epoxidation of styrene was observed until 80% of the cumene hydroperoxide had been converted. The selectivity of the cumene hydroperoxide consumption for styrene oxide formation ranged from 70 to 90% for different concentrations of cumene hydroperoxide and MoSe_2 . The rate at which styrene oxide formed was found to increase as the amount of catalyst was increased to 6 g/l, after which the reaction rate ceased depending on the amount of heterogeneous contact. The catalytic activity of molybdenum compounds in the styrene epoxidation process was found to depend on the nature of the ligand and to increase as follows: $\text{MoSi} < \text{MoS}_2 < \text{MoSe}_2$. The nature of the mechanism of epoxidation on WSe_2 was found to be analogous to that on MoSe_2 . As expected, however, WSe_2 turned out to be a less effective and less selective epoxidation catalyst than MoSe_2 . This lesser effectiveness of WSe_2 was attributed to its weaker electron-acceptor properties and to the decrease in the steady-state concentration of RO_2^\cdot radicals in the presence of WSe_2 because of the destruction of the peroxide radicals that occurs during the reaction process. Figures 3; references 12: 11 Russian, 1 Western.

The Effect of the Reaction Medium on the State of the Active Components of Ni-Cu Catalysts. I. Ni-Cu, Ni-Cu-Al, and Ni-Cu-Al-Ca Catalytic Systems

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[Article by M.G. Chudinov, B.N. Kuznetsov, V.N. Yefremov, Ye.Z. Golosman, A.M. Alekseyev, and V.I. Yakerson, State Scientific Research Institute of the Nitrogen Industry and Organic Synthesis Products, Moscow; Novomoskovsk Affiliate, State Scientific Institute of the Nitrogen Industry and Organic Synthesis Products; and Organic Chemistry Institute imeni N.D. Zelinskiy, Moscow; UDC 542.973:542.943'941:541.183:546.74'621'56'41:541.53:543.422]

[Abstract] An examination was made of the effect that the reaction medium has on the state of the active components of Ni-Cu, Ni-Cu-Al, and Ni-Cu-Al-Ca catalysts. The study catalysts were prepared by mixing powders of Ni and Cu hydroxocarbonates (specimens 1 through 3) and aluminum hydroxide (specimen 4) with a 25% aqueous solution of ammonia at 70° for 1 hour. The study specimens were then dried at a temperature of 100° and roasted for 5 hours at 400°. The fifth study specimen was prepared by adding aluminocalcium cement to the catalytic mass and subjecting it to hydrothermal treatment in distilled water at 85° for 1.5 hours followed by drying at 100° and roasting at 400°. The compositions of

the study catalyst systems were as follows (%): catalyst 1: 24.4 NiO and 75.6 CuO; catalyst 2: 49.4 NiO and 50.6 CuO; catalyst 3: 76.7 NiO and 23.3 CuO; catalyst 4: 39.5 NiO, 16.3 CuO, and 44.2 Al_2O_3 ; and catalyst 5: 27.1 NiO, 9.5 CuO, and 50.8 Al_2O_3 . The surfaces of the study catalysts were studied by x-ray photoelectron spectroscopy. All of the oxygen hydrogenation reactions were studied under atmospheric pressure in a continuous-type reactor. The gas mixture at the entrance contained 2-3% O_2 , 7% H_2 , and the rest N_2 . The temperature at which a 50% degree of conversion of O_2 was achieved was taken as a measure of activity. The studies performed established that the ratio of the surface concentrations of nickel and copper ($K = [\text{Ni}]/[\text{Cu}]$) increases upon the reduction of the study systems' copper-containing components and decreases when Ni^0 is formed. Oxidation treatment of the reduced specimens was found to be accompanied by an increase in K in the case of oxidation of nickel and by a decrease in the case of oxidation of copper. Exposure of the reduced Ni-Cu-Al and Ni-Cu-Al-Ca specimens in the reaction mixture (300°) was found to result in an increase in K to a constant value, with the Cu^0 changing partially into Cu^+ and Cu^{2+} . After surface treatment by the reaction medium the nickel was in an Ni^{2+} state. Figures 3; references 12: 8 Russian, 4 Western.

The Effect of the Reaction Medium on the State of the Active Components of Ni-Cu Catalysts. II. Ni-Cu-Al-Ca Catalysts of the Hydrogenation of Oxygen

927M0197H Moscow KINETIKA I KATALIZ
in Russian Vol 33 No 1, Jan-Feb 92 (manuscript
received 3 May 90) pp 147-151

[Article by B.N. Kuznetsov, V.N. Yefremov, M.G. Chudinov, Ye.Z. Golosman, G.M. Tesakova, A.M. Alekseyev, and V.I. Yakerson, State Scientific Research Institute of the Nitrogen Industry and Organic Synthesis Products, Moscow; Novomoskovsk Affiliate, State Scientific Research Institute of the Nitrogen Industry and Organic Synthesis Products; and Organic Chemistry Institute imeni N.D. Zelinskiy, USSR Academy of Sciences, Moscow; UDC 542.973:542.941:541.183:546.74'62'56'41:541.53:543.422]

[Abstract] An examination was made of the surface state of the active Ni and Cu components in type NKO-2 Ni-Cu-Al-Ca catalysts of the hydrogenation of oxygen when they are reduced in H_2 and during flooding of the reaction mixture. An Eskalab-5 x-ray photoelectron spectrometer was used to study three samples of type NKO-2 catalyst. The study catalysts were prepared by chemical mixing of nickel and copper hydroxocarbonates with aluminocalcium cement in the presence of an aqueous solution of ammonia (specimen NKO-2-1) and vapor condensate (NKO-2-2) at a temperature of 70 to 80°C with constant stirring. The stirring was continued until a 20-30% moisture level was achieved in the mass. Next, the product was roasted at 400°, mixed with graphite, and molded into tablet form. In the case of the

third specimen (NKO-2-3), nickel and copper hydroxocarbonates were mixed with aluminum hydroxide in the presence of an aqueous solution of ammonia at 70-80° with constant stirring until a 20-30% moisture level was achieved and then roasted at 400°. The effects of the reaction medium on the three catalysts were studied at temperatures ranging from 100 to 650°. The starting NKO-2-3 catalyst contained the following (%): NiO, 27.1; CuO, 9.5; Al₂O₃, 50.8; and CaO, 12.6. Studies of the change in the [Ni]/[Cu] ratio on the catalysts' surface as a function of reduction temperature established that the said ratio begins to increase at 150° because of the reduction of the copper and subsequent migration of the copper. After 400°, the [Ni]/[Cu] ratio begins to decrease on account of the reduction of the nickel and a reverse process of segregation of copper on the surface. These processes were most pronounced in the catalysts produced by mixing with the aluminocalcium cement (where the reaction with the aluminocalcium carrier is higher than with the Al₂O₃). Among the catalysts produced by chemical mixing with cements, the water-and-ammonia method results in higher [Ni]/[Cu] ratios at elevated temperatures than when an aqueous medium is used. This difference was attributed to the different formation mechanisms and to the fact that a mixed nickel and copper hydroxoaluminate forms in the water-and-ammonia medium whereas copper oxide and nickel hydroxoaluminate forms in an aqueous medium. The reduction process was found to occur most easily in the NKO-2-3: The principal reduction process occurred between 180 and 400°, and the reduction peaks reached their maxima at 300 and 520°. The x-ray photoelectron studies performed confirmed that the hydrogenation of oxygen on NKO-2-3 at 300 and 520° will occur on surfaces with different compositions and, in all likelihood, according to different mechanisms. When the reaction mixture is flooded onto the NKO-2-3 Ni-Cu-Al-Ca catalyst at 300°, the [Ni]/[Cu] ratio increases sharply. The Ni²⁺ and copper are in difference charge stages on the catalyst surface (Cu⁰, Cu⁺, Cu²⁺). At 520°, on the other hand, the [Ni]/[Cu] ratio remains unchanged. The catalyst surface is enriched with copper, the copper is in a Cu⁰ state, and the nickel is partly in an Ni⁰ state and partly in an Ni²⁺ state. Figures 4; references 10: 8 Russian, 2 Western.

Carriers for Organic Synthesis Catalysts. III. Strength Characteristics of Aluminum Oxides Produced by Heat-Treating γ -Al₂O₃

927M01971 Moscow KINETIKA I KATALIZ in Russian Vol 33 No 1, Jan-Feb 92 (manuscript received 5 Dec 90) pp 190-196

[Article by B.M. Fedorov, V.I. Nekhoroshev, I.A. Zhukov, and A.S. Berenblyum, All-Union Scientific Research Institute of Organic Synthesis, Moscow; UDC 542.975:546.623-31:542.46:539.4.01]

[Abstract] The strength characteristics of a roasted γ -Al₂O₃ carrier (A-64K) as a function of heat treatment conditions were examined. Specimens of the commercial

carrier A-64K (produced at the Ryazan Oil Refinery) were roasted for between 1 and 16 hours at temperatures of 550 to 1,350° as described elsewhere. The specimens' strength characteristics were determined by several techniques: splitting with a knife with a 0.1 mm cutting edge, crushing along the generatrix, and rubbing to determine the amount of abrasive wear. Within the temperature interval studied, the specimens' strength characteristics were found to vary rather widely and in an extremely complex manner. The temperature dependence plotted for the study temperature interval was quite complex with several maxima and minima. This led the researchers to conclude that the nature of the temperature dependences derived during the experiments is linked to the processes occurring in the pore structure of the granules during the course of their heat treatment. The reasons for the appearance of each of the maxima and minima discovered are discussed in detail along with the temperature bounds of the sintering of the different aluminum oxide phases in accordance with surface-diffusion and viscous-flow mechanisms. Figures 2; references 20: 17 Russian, 3 Western.

The Effect of Volatile Molybdenum Compounds on the Catalytic Properties of Iron-Molybdenum and Iron Oxide Systems

927M0197J Moscow KINETIKA I KATALIZ in Russian Vol 33 No 1, Jan-Feb 92 (manuscript received 5 Apr 91) p 253

[Article by A.V. Demidov, I.G. Danilova, and B.I. Popov (deceased), Catalysis Institute, Siberian Department, USSR Academy of Sciences, Novosibirsk; UDC 541.128.3:542.943.7:546.776'723-31:547.26]

[Abstract] It has been reported elsewhere that the reaction of selective oxidation of MeOH on Mo-containing catalysts entails the reaction of MoO₃ (up to 40 wt.-% in the catalyst) and MeOH with the formation of volatile MO compounds that in turn react with the catalyst. The authors of this letter to the editor investigated the effect of these volatile compounds on the yield (y) and selectivity (S) with respect to the formaldehyde of MeOH vapors passed through a layer of MoO₃ and catalyst (6.5 vol.-% MeOH, $\tau = 0.3 \text{ s}^{-1}$). A significant increase in the activity of the Fe-Mo systems was observed. In the case of Fe₂(MoO₄)₃·2MoO₃ at a temperature of 300 K with a grain size of 0.5 to 1 mm, for example, y increased to 74% (versus 60% under standard conditions). In the case of Fe₂(MoO₄)₃·2MoO₃ at a temperature of 300 K but with a grain size of 4 x 4 mm, y increased from 65% (under normal conditions) to 72%. In the case of CrFe(MoO₄)₃·2MoO₃ at a temperature of 300 K with a grain size of 4 x 4 x 2 mm, y increased from 66% to 79%. The values achieved for S for all three of the above Fe-Mo catalysts decreased slightly. In the case of iron oxide alone, however, high values of both S and y were seen. Specifically, for Fe₂O₃ at a reaction temperature of 250 K, values of 45 and 91% were found for y and S, respectively (as opposed to values of 0% in both cases under standard conditions). At 300 K, the values of y

and S found for Fe_2O_3 were 77 and 86%, respectively (once again, as opposed to 0% for both γ and S under standard conditions). Table 1; reference 1 (Russian).

Chromatography-Mass Spectroscopy Study of Byproducts Obtained in Catalytic Amination of Fatty Alcohols

927M0235E St. Petersburg ZHURNAL PRIKLADNOY KHIMII in Russian Vol 65 No 1, Jan 92 (manuscript received 2 Aug 90) pp 171-174

[Article by L. I. Virin, A. N. Boguslavskiy, V. A. Filimonov, I. Yu. Popova, B. A. Suvorov, V. I. Kolbasov, O. V. Klyuyeva, Moscow Scientific Production Association "Syntez"; UDC 543.51:547.51]

[Abstract] Production of alkylamines doubled in the past ten years, the principal production method being catalytic amination of fatty alcohols over copper oxide catalysts in presence of hydrogen. The mechanism of the overall reaction has been adequately studied, but little is known about the side reactions and the composition of the byproducts. In this work, amination of n-dodecyl alcohol was investigated over IKT-12-6 and 61PKh 114M catalysts at 175-300°. Thirteen byproducts were identified by means of their chromatographic separation and mass-spectroscopic data. Formation of the nitriles

over IKT-12-6 catalyst occurred only at high temperatures, over the 61PKh 114M the reaction occurred at lower temperature. Table 1; figure 1; references 8: 4 Russian, 4 Western.

Flow Pattern Through a Series of Catalyst Blocks With Honeycomb Pattern

927M0235G St. Petersburg ZHURNAL PRIKLADNOY KHIMII in Russian Vol 65 No 1, Jan 92 (manuscript received 30 Jul 91) pp 225-227

[Article by A. V. Bespalov, Moscow Chemical-Technical Institute imeni D. I. Mendeleyev; UDC 661:532.546]

[Abstract] Several arrangements are possible for block catalyzers of the honeycomb pattern. The blocks themselves may be of a massive structure penetrated with multiple channels. In general the blocks should be placed at a small angle to the axis of the principal flow of the reactants so that heat transfer could be facilitated cross the flow along with adequate mixing of the components. Experiments were carried out testing these concepts and it was concluded that shifting the block positions in respect to the main flow direction increased the accessibility of the internal surface of block channels and hence extended their utilization. Figures 2; references: 9 (Russian).

The Electrochemical Properties of Molybdenum Dithiocarbamates—Antioxidants of Hydrocarbons

927M0182C Moscow NEFTEKHIMIYA in Russian
Vol 32 No 1, Jan-Feb 92 (manuscript received
26 Sep 91) pp 25-28

[Article by T.A. Zaymovskaya, G.N. Kuzmina, O.P. Parenago, and M.Ye. Niyazymbetov, Petrochemical Synthesis Institute imeni A.V. Topchiyev, USSR Academy of Sciences, Moscow; UDC 621.892.86.84:546.77]

[Abstract] The electrochemical properties of molybdenum dithiocarbamates that act as antioxidants when used with hydrocarbons were examined. The synthesis of the new molybdenum dithiocarbamates was described in previous communications. In the present communication, the authors report the results of voltammetric measurements and an electrolysis experiment to which the new compounds were subjected. Three different molybdenum dithiocarbamates were studied: dimolybdenum (V) di- μ -oxosulfo-dioxo-di-n-butylthiocarbamate (1), di-molybdenum (V) di- μ -sulfo-disulfo-di-n-butylthiocarbamate (2), and molybdenum (VI) oxosulfodi-2-ethylhexylthiocarbamate (3). Each of the new molybdenum dithiocarbamate complexes was placed in a glass cell (volume, 27 ml) whose cathode and anode spaces were separated by a glass filter. A rotary disk platinum electrode and P-5827M potentiostat were

used to take polarization measurements. A current integrator designated at the Organic Chemistry Institute of the USSR Academy of Sciences was used to take the coulometric measurements. All of the voltammetric measurements were taken in absolute acetonitrile in a background of 0.1 N $(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$ in an argon atmosphere. The electrolysis process was performed in the same medium. $\text{Ag}/0.1\text{Ag}^+$ in acetonitrile served as the comparison electrode. The working concentrations of depolarizer during the voltammetric measurements ranged from 0.01 to 0.05 mol/l. The $(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$ salt was dried out in a vacuum over P_2O_5 . The studies performed established that the values of the half-wave potentials of the oxidation and reduction of the molybdenum dithiocarbamate complexes depend on the structure of the said complexes and correlate with their antioxidant properties. The regeneration of each of the three molybdenum dithiocarbamate complexes studied during cathode electrolysis confirmed the complexes' repeated participation in the decomposition of hydrogen peroxide in accordance with a mechanism whose first stage entails the oxidation complexing of hydrogen peroxide to the complex. The hydrogen peroxide activated in this manner then decomposes, and the three molybdenum dithiocarbamates are regenerated in their initial valence state and participate in the cycle once more. This hypothesis was confirmed by the value of the stoichiometric inhibition of 6 that was obtained for the complex from which a "regenerated" complex 3 was eventually produced. References 11: 7 Russian, 4 Western.

Possibility of Determining Algal Kerogen Precursor from Its Ozonolysis Products

927M0195A Moscow *KHIMIYA TVERDOGO TOPLIVA* in Russian No 2, Mar-Apr 92 (manuscript received 28 Feb 91) pp 5-8

[Article by A. N. Yegorkov, Industrial Hygiene SRI (AU); UDC 552.574.22:542.943.5]

[Abstract] The majority of current researchers are leaning toward acknowledgement of algal origin of shale kerogen. However, the problem of kerogen genesis is complex and comprises many various aspects affecting the conversion of algae components during kerogen formation. One such aspect is to what extent the chemical structure of kerogen reflects the algal precursor, specifically, the possibility of identifying an algal precursor from its kerogen structure. In the present work it was demonstrated that the algal precursor of the organic matter in sapropelite in some cases may be determined from the composition of acetic acid ozonolysis of kerogen without applying data from petrographic analysis. Figure 1; References 15: 8 Russian, 7 Western.

Biologically Active Substances of Brown Coal

927M0195B Moscow *KHIMIYA TVERDOGO TOPLIVA* in Russian No 2, Mar-Apr 92 (manuscript received 05 Aug 91) pp 28-34

[Article by I. V. Aleksandrov, G. I. Kandelaki, T. N. Zarifova, and Yu. A. Vazhova, Chemical Technology Institute imeni D. I. Mendeleev, Moscow; UDC 665.7.032.54]

[Abstract] Utilization of brown coals for non-fuel purposes is well known. Preparations derived from the humic constituents of peat and brown coal and blended with mineral fertilizers are used more and more widely to increase agricultural output. Research shows that it is possible to obtain effective organic-mineral fertilizers having many desirable properties. In the present work genetically young brown coals of the Adunchulun deposit of the Mongolian People's Republic and the Tyulgan deposit of the southern Urals basin were used as an example to demonstrate the possibility of deriving plant growth stimulants from these coals by oxidative-hydrolytic destruction. The contents of micro-, macro-, and toxic elements in the initial Tyulgan coal as well as the water-soluble products of nitric acid and hydrogen peroxide oxidation were determined. Figures 2; references 4 (Russian).

Effect of Degree of Surface Oxidation of Natural Coals on Rheological Properties of Highly Concentrated Water-Coal Suspensions

927M0195C Moscow *KHIMIYA TVERDOGO TOPLIVA* in Russian No 2, Mar-Apr 92 (manuscript received 16 Jul 91) pp 39-42

[Article by A. A. Larina and A. S. Makarov, Colloidal Chemistry and Hydrochemistry Institute, Kiev; UDC 541.183:622.333+622.693]

[Abstract] The problems of creating highly concentrated water-coal suspensions having predetermined structural and mechanical properties is directly related to the formation of adsorption layers. The latter are largely determined by the properties of the dispersion medium and the characteristics of the coal, i.e. stage of metamorphism, ash and minerals content, and chemical nature of the surface. By altering the surface properties of the coals it is possible to affect the formation of adsorption layers and therefore the properties of concentrated water-coal suspensions. In the present work a study was made of the mechanism of the diluting action of a number of additives as a function of the degree of surface oxidation of Kuzbass coals. Rheological characteristics and sedimentation stability of the suspensions prepared by wet milling plain and oxidized coals were also studied. It was demonstrated that oxidation of the surface significantly alters the rheological characteristics of the suspensions. Figures 3; references 5 (Russian).

Methodological Recommendations for Evaluating Ecological-Economic Effectiveness of Chemical-Technological Systems

927M0196A Kiev *KHIMICHESKAYA TEKHOLOGIYA* in Russian No 1(181), Jan-Feb 92 (manuscript received 18 May 91) pp 90-93

[Article by Yu. V. Yevdokimov, V. A. Shlepchenko, and E. A. Svertilov, Gas Institute, Kiev; UDC 577.47.008.66]

[Abstract] The development of modern industrial production placed a burden on the interrelationship between society, industry, and nature. Each year 146,000,000 tons of sulfur dioxide, 250,000,000 tons of dust, and 70,000,000 tons of harmful gases are emitted to the atmosphere and 32 km³ of raw wastes enter the water systems. Damage resulting from environmental pollution is on the order of 5 percent of gross national product in many advanced countries. In its struggle with pollution, society is obliged to lay out considerable amounts of materials and resources. For example, capital expenditures for environmental protection comprise 5 to 20 percent of total capital investment. Most dangerous in the ecological sense are industries such as

metallurgical combines and other such chemical technological plants. In the present work the theoretical premises for formulating effectiveness criteria for chemical-technological systems are discussed. An ecological-economic criterion is proposed and formulas are presented for calculating it at all levels in the life cycle of chemical-technological systems. Theoretical premises are illustrated with a concrete example of a waste-free system for treating furnace off gases in aluminum production. References 4 (Russian).

Study of Technical-Economic Indices of Coal-Gas Transport Systems

927M0196B Kiev *KHIMICHESKAYA*

TEKHNOLOGIYA in Russian No 1(181), Jan-Feb 92 (manuscript received 13 May 91) pp 93-95

[Article by T. S. Dzhigirey and A. P. Klimenko [deceased], Gas Institute, Kiev; UDC 621.547.66.012.7]

[Abstract] Coal can be transported from Siberia by either pipeline or rail. If the pipeline is hydraulic, water or carbon dioxide is added to the coal dust. If the pipeline is pneumatic, the coal dust may be transported with natural gas, air, or some other gas carrier. In the present work a preliminary technical-economic evaluation is presented for coal dust pipeline systems which takes into account the preparation and storage of the coal dust, carbon dioxide production, preparation and separation of suspensions, loading the coal dust into the pipeline, and pumping stations. Pipeline transport is compared with rail by specific cost outlays. Coal-gas transport using liquid carbon dioxide is twice as costly as other methods of transport. While hydraulic transport may be less costly, about 4 percent of the coal dust is expended at the terminal to evaporate the water.

Automated System for Simulating Reproduction Processes for Planning Capital Investment in Sectors

927M0196C Kiev *KHIMICHESKAYA*

TEKHNOLOGIYA in Russian No 1(181), Jan-Feb 92 (manuscript received 12 May 91) pp 96-98

[Article by D. A. Bochkov, V. N. Kissel, and A. M. Baryshnikov, Steel and Alloys Institute, Moscow; UDC 66.045]

[Abstract] The basic difficulty in the process of planning capital investments lies in the necessity to regulate sector development with the macroeconomic indices while still taking into account the technical status of concrete projects. Therefore, an automated system of making decisions in investment policy together with a model simulating reproduction processes of basic funds for sectors includes an information system which characterizes the structure and make-up of the fixed capital of the sectors. In the present work conceptual problems on modeling reproduction processes for planning sector capital investment are examined. This is a problem for

nonlinear programming with a large number of unknowns. Solution using standard methods presents significant difficulties, and a heuristic algorithm was developed. A general modeling scheme is presented along with variants for using modeling subsystems in the process of making decisions with the aid of heuristic algorithms.

Continuous Hydrogenation of Furfural Over Suspended and Stationary Alloy Catalysts

927M0231A Moscow *KHIMICHESKAYA*

PROMYSHLENNOST in Russian No 4, Feb 92 pp 200-202

[Article by T. B. Beysekov, A. Ye. Bitemirova, V. A. Lapshin, A. M. Kuatbekov, A. Meldeshov; UDC 66.094.17:[661.7:547.724.1]

[Abstract] Multicomponent alloyed copper catalyst in a suspended or stationary state was investigated in continuous hydrogenation of furfural. The catalyst contained: Cu-50%, Al- 5%, FC-2% FS (FC -ferrochrom containing 69.1% Cr, 29.94% Fe, 0.96% impurities; FS- ferrosilicon with 49.19% Si, 30.48% Cr, 20.22% Fe, 0.11% impurities) was used in 2, 3 and 5% suspension and compared with a standard GIPKh-105 material showing that the alloy catalyst outperformed the standard catalyst. When a freshly distilled furfural stabilized with phenoan 30 was hydrogenated at 80-140° C over stationary catalyst listed above, the furfuryl alcohol was obtained in 98.5-100% yield and the catalyst was active for a period of 580 hrs. Table 1; figures 1; references 17: (Russian, 5 by Western authors).

Synthesis of Magnetic Iron Oxide Powders by Liquid Phase Oxidation of Iron Pentacarbonyl With Ozone

927M0235A St. Petersburg *ZHURNAL PRIKLADNOY*

KHIMII in Russian Vol 65 No 1, Jan 92 (manuscript received 27 Mar 91) pp 29-33

[Article by M. L. Perepletchikov, I. I. Didenkulova, Yu. A. Aleksandrov, Nizhnegorod State University imeni N. I. Lobachevskiy; UDC 546.214;546.725;546.723*722-31]

[Abstract] Ferromagnetic powders of iron oxide are used widely in production of magnetic tapes and disks, magnetic fluids, ferrites, etc. The kinetics of exhaustive oxidation of $\text{Fe}(\text{CO})_5$ with ozone was investigated in a number of solvents inert to iron pentacarbonyl: a binary acetone-water mixture, perfluorodecaline, perfluoro polyether and methyl acetate. It was shown that the kinetics of this reaction was of the first order in respect to both ozone and $\text{Fe}(\text{CO})_5$. The product of this reaction was amorphous to x-rays and non-ferromagnetic Fe_2O_3 . When this product was heated above 290-300° it converted to Fe_3O_4 and became magnetic. This oxidation of $\text{Fe}(\text{CO})_5$ to Fe_3O_4 was quantitative. Table 1; figures 3; references 5: 4 Russian, 1 Western.

Vanadium (V) Peroxocomplexes in Catalysis of Conversions of Hydrogen Peroxides in Trifluoroacetic Acid

927M0180A Moscow KOORDINATSIONNAYA KHIMIYA in Russian V 18, N 1, Jan 92 (manuscript received 14 Aug 91) pp 3-25

[Article by A. Ye. Gekhman, N. I. Moiseyeva and I. I. Moiseyev, Institute of General and Inorganic Chemistry imeni N. S. Kurnakov AS USSR, Institute of Chemical Physics imeni N. N. Semenov AS USSR; UDC 541.128:542.92:546.215:545.214]

[Abstract] A study of the effect of the medium on the decomposition of peroxides and study of the reactivity of intermediately forming complexes in relation to organic substrates showed that vanadium (V) complexes in trifluoroacetic acid effectively catalyzed decomposition of hydrogen peroxide with formation up to 15 percent of ozone. During interaction with peroxide trifluoroacetic acid, vanadium compounds catalyzed not only its decomposition with oxygen but also decarboxylation. A $V(V)-H_2O_2-CF_3COOOH$ catalytic system made it possible to oxidize quickly such scarcely-oxidizable compounds as internal and cyclic perfluoroolefins, hexafluorobenzene and other compounds. This system displayed the unusual capacity of selectively oxidizing a substrate of one nature in the presence of a substrate of another nature. The effect of oxidizable substrates on the quantity of ozone being given off was discussed. Kinetic methods showed that, in the $V(V)-H_2O_2-CF_3COOOH$ system, sequential reactions of the catalyst with an oxidation agent formed some active vanadium (V) complexes, responsible for oxidation of all of the compounds studied and liberation of ozone. Both hydrogen peroxide and peroxytrifluoroacetic acid participated in formation of these complexes. All regularities detected were explained by a model, which includes an intraspherical regrouping of 2 peroxoligands into the (O_3^{2-}) grouping. A mathematical model describing oxidation of the substrates and ozone formation was constructed. References 36: 22 Russian; 14 Western.

Crystalline Structure of Hydrate of Cesium Pentafluorozirconate

927M0180C Moscow KOORDINATSIONNAYA KHIMIYA in Russian V 18, N 1, Jan 92 (manuscript received 12 Jul 91) pp 38-41

[Article by V. V. Tkachev, R. L. Davidovich, et al.; Institute of Chemical Physics imeni N. N. Semenov, AS USSR, Institute of Chemistry DVO, AS USSR; UDC 548.736.5:546.831'161]

[Abstract] A study of the crystalline structure of $CsZrF_5 \cdot xH_2O$, performed to obtain new data concerning the structure of pentafluorozirconates and to establish the nature of structural transformations in some cesium fluoro-zirconates, showed that the crystalline structure is constructed from infinite ionic chains with $(ZrF_5H_2O)_n^{n-}$ composition oriented along axis c and Cs^+

cations, situated between the chains. The polymer chains were composed of $ZrF_7(H_2O)$ polyhedrons with a configuration of a distorted dodecahedron and common F-F edges connected to each other. The Zr-F distance lies in the 2.00-2.25 Angstroms interval and the length of the bond $Zr-O(H_2O)$ equals 2.31 Angstroms. The $CsZrF_5 \cdot xH_2O$ crystalline structure is similar to the $(NH_4)ZrF_5 \cdot xH_2O$ structure. References 7: 5 Russian; 2 Western.

Crystalline Structure of New Cesium Fluorozirconate $Cs_5Zr_4F_{21} \cdot 3H_2O$

927M0180D Moscow KOORDINATSIONNAYA KHIMIYA in Russian Vol 18, No 1, Jan 92 (manuscript received 22 Aug 91) pp 42-47

[Article by V. V. Tkachev, R. L. Davidovich and L. O. Atovmryan, Institute of Chemical Physics N. N. Semenov, AS USSR; Institute of Chemistry DVO, AS USSR; UDC 548.736.5:546.832'161]

[Abstract] Determination of the crystalline structure of a new cesium fluoro-zirconate showed it to be constructed from Cs^+ cations and complex tetrameric anions $[Zr_4F_{21}(H_2O)_3]^{5-}$, each of which was composed of 4 zirconium polyhedrons, linked by common F-F edges in a chain. The lengths of the terminal $Zr-F_t$ bonds were changed in the 1970-2053 Angstroms interval and the lengths of the $Zr-F_b$ bridge bonds lay within the 2093-2255 Angstroms interval. Coordination molecules of H_2O were removed from the zirconium atoms by 2270, 2332 and 2316 Angstroms. A tetrameric chain anion $Zr(1)F_7-Zr(2)F_7(H_2O)-Zr(3)F_7(H_2O)-Zr(4)Fe_6(H_2O)$ containing 3 zirconium polyhedrons of different compositions was established for the first time. Figures 2; references 7 (Russian).

New Rubidium and Cesium Fluorozirconates and Fluorohafnates

927M0180E Moscow KOORDINATSIONNAYA KHIMIYA in Russian Vol 18, No 1 Jan 92 (manuscript received 22 Aug 91) pp 48-55

[Article by R. L. Davidovich, V. B. Logvinova and L. V. Teplukhina, Institute of Chemistry DVO AS USSR; UDC 541.49:546.83'161]

[Abstract] A study of the interaction in an aqueous solution of MF and $(H_3O)_2ZrF_6$ ($(H_3O)_2HfF_6$) and MCl and $(H_3)_2ZrF_6$ ($(H_3)_2O_2HfF_6$) in a wide interval of molar ratios of components was described and discussed. Conditions of production of hydrates of rubidium pentafluorozirconates and pentafluorohafnates were established. Previously unknown fluoro-zirconates and fluorohafnates of rubidium and cesium with composition of $Rb_5Zr_4F_{21} \cdot 3H_2O$, $Cs_5Zr_4F_{21} \cdot 3H_2O$, $Rb_5Hf_4F_{21} \cdot 3H_2O$ and $Cs_5Hf_4F_{21} \cdot 3H_2O$ were synthesized. Radiographic, infra-red spectrographic and thermogravimetric studies showed that the compounds $Rb(Cs)ZrF_5 \cdot xH_2O$ and $RbHfF_5 \cdot xH_2O$ described in the literature represent

$M_5A_4F_{21} \cdot 3H_2O$ and compound $CsHfF_5 \cdot xH_2O$ represents $Cs_6Hf_5F_{26} \cdot 4H_2O$. Figures 2; references 12: 10 Russian; 2 Western.

The Crystalline Structure of Aminoguanidinium (+1) Pentafluorozirconate

927M0181A Moscow KOORDINATSIONNAYA
KHIMIYA in Russian Vol 18 No 6, May 92
(manuscript received 26 Nov 91) pp 576-579

[Article by B.V. Bukvetskiy, A.V. Gerasimenko, and R.L. Davidovich, Chemistry Institute, Far Eastern Department, Russian Academy of Sciences; UDC 548.736.5:546:831'161]

[Abstract] The authors of the study reported herein examined the crystalline structure of $(CN_4H_7)ZrF_5$. The study aminoguanidinium (+1) pentafluorozirconate was synthesized by reacting $(CN_4H_7)Cl$ and $(H_3O)_2ZrF_6$ in a 1:1 molar ratio. The study monocrystals were obtained by slow crystallization from a saturated solution at room temperature. A DAR UMBk automatic diffractometer (MoK α radiation, graphite monochromator, 791 independent and nonzero reflexes) was used to perform the analysis. The $(CN_4H_7)ZrF_5$ study crystals were found to be rhombic and to be characterized by the following parameters: $a = 6.640(1)$, $b = 6.875(1)$, and $c = 15.999(2)$ angstroms; $Z = 4$; and limiting boundary, $Pnma$. $(CN_4H_7)ZrF_5$ crystals were determined to be formed of autonomous infinite $(ZrF_5)^{2-}$ chains directed parallel to one another along the x coordinate axis with aminoguanidinium (+1) cations located between the chains. The lengths of the end bonds in the ZrF_5 polyhedra were found to equal 1.944(2), 1.944(2), and 1.957(2) angstroms, and the lengths of the bridge bonds were found to equal 2.108(2), 2.128(2), 2.137(2), and 2.178(2) angstroms. The shortest F-F distance in the polyhedron is the F-F distance between the fluorine bridge atoms F(1)-F(2) (2.340 angstroms). The remaining F-F distances range from 2.493 to 2.916 angstroms. The $(CN_4H_7)ZrF_5$ crystalline structure is said to be the first example of a fluorozirconate structure containing polymer chains formed as a result of the joining of heptacoordinate zirconium polyhedra by means of common ribs. Figure 1, tables 3; references 4 (Russian).

Diethylenetriamine Pentaacetate Complexes of Zirconium and Hafnium

927M0181B Moscow KOORDINATSIONNAYA
KHIMIYA in Russian Vol 18 No 6, May 92
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[Article by R.L. Davidovich, V.B. Logvinova, and L.V. Teplukhin, Chemistry Institute, Far Eastern Department, Russian Academy of Sciences; UDC 541.49:546.83]

[Abstract] A series of diethylenetriamine pentaacetate complexes of zirconium and hafnium were synthesized.

To synthesize the new complexes, the researchers dissolved equimolar quantities (0.0125 mole each) of $AOCl_2 \cdot 8H_2O$ ($A = Zr, Hf$) and H_5 Dtpa by heating in 400 ml H_2O . Next, small portions of alkaline metal or guanidinium carbonates were stirred into the transparent solution in amounts corresponding to the molar ratio $M_2CO_3:AOCl_2 \cdot 8H_2O$ 0.5:1. The pH of the solution was increased from 1.5 to 2. The new diethylenetriamine pentaacetate complexes of zirconium and hafnium were found to have an exceedingly high solubility in water and to be precipitated from very concentrated solutions. The only diethylenetriamine pentaacetate complexes of Zr and Hf that could be produced in a crystalline state were complexes with potassium and guanidinium cations. The researchers were unable to precipitate the respective complexes with Li^+ , Na^+ , and Cs^+ cations because the solution was transformed into a vitriform mass after standing for any extended period. The following complexes were synthesized: $KZrDtpa \cdot 3H_2O$, $KHfDtpa \cdot 3H_2O$, $(CN_3H_6)ZrDtpa \cdot 3H_2O$, and $(CN_3H_6)HfDtpa \cdot 3H_2O$. The complexes were subjected to elemental and x-ray analysis, IR spectroscopy, and thermogravimetric analysis in accordance with the established procedures. The new compounds were colorless crystals that remain stable in air and highly soluble in water. The H_2O molecules in $MADtpa \cdot 3H_2O$ were comparatively weakly bound. Dehydration of the complexes occurred at temperatures between 80 and 150°C. The dewatered compounds quickly absorbed atmospheric moisture and returned to their initial hydrated state. The IR spectroscopy studies performed demonstrated that the $Dtpa^{5-}$ anion acts as an octadentate ligand in the new compounds. X-ray analysis established that the new diethylenetriamine pentaacetate complexes of zirconium and hafnium with one and the same cation in their outer sphere are isostructural. The $KADtpa \cdot 3H_2O$ crystals were determined to be triclinic, while the $(CN_3H_6)ADtpa \cdot 3H_2O$ compounds were found to be monoclinic. Tables 6; references 7: 4 Russian, 3 Western.

The Formation, Composition, and Stability of Fluoride Complexes of the Ion Fe^{3+} on the Surface of Iron Oxide (III)

927M0181C Moscow KOORDINATSIONNAYA
KHIMIYA in Russian Vol 18 No 6, May 92
(manuscript received 12 Apr 91) pp 610-613

[Article by V.N. Volkov, M.L. Davtyan, B.I. Lobov, and L.A. Rubina, Pskov State Pedagogical Institute; UDC 546.621.541.183.546.72]

[Abstract] The authors of the study reported herein used the method of heterogeneous pH-metric titration to determine the staged formation constants of fluoride complexes of iron oxide (III) on the surface of $\alpha-Fe_2O_3$. They hypothesized that a doubly charged $(-O-)Fe^{2+}$ complex participates in the reaction with the fluoride ions in the initial points of the titration curve, whereas the singly charged complexes $(-O-)FeF^+$ and $(-O)_2Fe^+$ enter into the reaction in the following stage. The constants of

the two stages were determined as follows: $\lg K_1 = 4.04$, and $\lg K_2 = 3.37$. These constants virtually coincided with the corresponding staged formation constants of fluoride complexes of Fe (III) in an aqueous solution that were published by Sillen and Martell (i.e., $\lg K_1 = 5.18$, $\lg K_2 = 3.95$, and $\lg K_3 = 2.77$). The authors of the present study took this as confirmation of their hypothesis that a surface complex with a charge of 2+ first enters into the complexing reaction with the F^- ion. The higher value of K_2 as compared with K_3 was linked to the dehydration of the surface having a zero charge and with a positive change in entropy. Figure 1, table 1; references 6: 5 Russian, 1 Western.

Precipitation of Crystal Hydrates of Acetylacetonates as a Method of Purifying Rare Earth Elements of Calcium (by Way of the Example of Neodymium)

927M0181E Moscow KOORDINATSIONNAYA KHIMIYA in Russian Vol 18 No 6, May 92 (manuscript received 15 Oct 91) pp 649-653

[Article by Zoan An Tu, N.P. Kuzmina, L.I. Martynenko, and G.N. Mazo, Moscow State University imeni M.V. Lomonosov; UDC 546.657+546.41:547.442.3]

[Abstract] The prospects of precipitation of crystal hydrates of acetylacetonate as a method of purifying rare earth elements to remove their calcium impurities were examined. The prospects of the precipitation technique were evaluated by way of the example of neodymium-calcium. A mixture of neodymium and calcium was produced from commercial preparations of $Nd(NO_3)_3 \cdot 6H_2O$ and $CaCl_2 \cdot 2H_2O$ (both of which bore a grade of "pure"). The acetylacetonate used also had a grade of "pure." The neodymium content of the study solutions and precipitates was determined by complexometric titration (with xylenol orange as an indicator). The calcium content of the solutions was determined by atomic-fluorescence spectroscopy with an AFS-2000 (Baird, United States) and by atomic-emission spectrometry on an ICP atomic-emission spectrum analyzer (also produced by Baird). The pH-metric titration was performed on a pH-673 with an aqueous solution of NaOH without CO_2 . Starting concentrations of Ca (II) and Nd (III) of 0.05 mol/l were used. The pH-metric titration studies performed established that at the chosen metal and ligand concentrations, CaA_2 forms in the pH range from 7 to 10, whereas NdA_3 forms at pH levels of 4.5 to 7.5. Experiments to separate the Ca and Nd were conducted with two series of starting solutions with different total concentrations of neodymium and calcium: 0.14 mol/l and 0.25 mol/l. The Nd^{3+} concentration in the mother liquors did not depend on its starting concentration and in all cases ranged from 1.5 to 3×10^{-3} mol/l. The completeness of neodymium precipitation, as judged by the ratio of the molar quantities of Nd^{3+} in the precipitate and in the starting mixture, ranged from 97 to 99%. The concentration of Ca^{2+} in the starting and mother solutions remained close. The experiments performed established that a pH of 8 results in effective

separation of neodymium and calcium. The experiments further established that the efficiency of separating neodymium and calcium may be increased by reprecipitation of the resultant acetylacetonate precipitates. The proposed method is quicker than the currently used technique of separating neodymium and calcium based on oxalate precipitation followed by ion-exchange separation. Although the new method is not very efficient in purifying mixtures with a rare earth element concentration below 1.5×10^{-2} mol/l, it yields good results in other cases. Figure 1, tables 2; references 10: 6 Russian, 4 Western.

Doping $YBa_2Cu_3O_x$ High-Temperature Superconductors With Lithium and Potassium

927M0183A Ashgabat IZVESTIYA AKADEMII NAUK TURKMENISTANA in Russian No 3, May-Jun 92 (manuscript received 19 Nov 90) pp 28-31

[Article by K.B. Sadykov, A. Berkeliyev, Sh. Meretliyev, O. Mosanov, A.R. Mikhaylov, N.G. Bekmedova, O.M. Kurbannazarov, and M. Serginov, Physics Engineering Institute, Turkmen SSR Academy of Sciences; UDC 538.945]

[Abstract] The effects of doping the high-temperature superconductor $YBa_2Cu_3O_x$ with lithium and potassium were examined. The high-temperature superconductors $YBa_2Cu_{3-x}Li_xO_y$ ($x = 0, 0.1, 0.3$, and 1.0) and $YBa_2-zK_zCu_3O_y$ ($z = 0.4$) were synthesized and simultaneously doped by the solid-phase reaction method. Stoichiometric quantities of Y_2O_3 , $BaCO_3$, CuO , Li_2CO_3 , and K_2CO_3 were mixed, ground, and roasted in a furnace in an oxygen stream at a temperature of 900 to 940° for 72 hours. The resultant specimens were ground a second time, molded, and subjected to annealing at 950°C for 36 hours, after which they were held at temperatures of 500 down to 450°C for 36 hours under the pressure of purified dry oxygen. The specimens' superconductivity was initially tested in a magnetic field with respect to Meissner's effect in liquid nitrogen. Next, specimens measuring about $12 \times 2 \times 1$ mm³ were cut from the ceramics. The electrical properties of those specimens were measured by the four-probe compensation method at a temperature of 77 to 300 K in forward and reverse thermal cycles. Direct currents of 0.5, 1.0, 5.0, 10, and 15 mA were passed through the specimens. The $YBa_2Cu_2LiO_y$ compounds produced did not manifest superconductivity at temperatures from 77 to 300 K. The potassium-doped compounds, which were doped by replacing a bivalent barium ion with a univalent potassium ion, became superconductive at 90 K. The researchers further established that specimens doped with univalent potassium will have heterovalent copper cations with electron exchange reactions occurring between them. The researchers concluded that while high-temperature superconductors produced by simple deviation from stoichiometry (a surplus of oxygen) have only limited stability, high-temperature superconductors produced by introducing the potassium ion into a specimen in accordance with Verwey's "checked valence"

mechanism are characterized by stable, technologically reproducible high-temperature superconductivity. The specimens synthesized and doped by the authors of this study have already retained their superconductivity for more than a year. Figure 1; references 19: 3 Russian, 16 Western.

Synthesis of Liquid Crystal Derivatives of Ferrocene and Their Complexes with Cu^{2+}

927M0194C Moscow IZVESTIYA AKADEMII NAUK
ROSSIYSKOY AKADEMII NAUK SERIYA
KHIMICHESKAYA in Russian No 2, Feb 92
(manuscript received 25 Jan 91) pp 402-407

[Article by Yu. G. Galyametdinov, O. N. Kadkin, and I. V. Ovchinnikov, Physical Technical Institute, Kazan; UDC 547.357.2+542.91:541.49:546.562+54-144]

[Abstract] Liquid crystals containing transition metals may have unusual electrical, magnetic, and optical properties. Introducing various transition metals into the mesogenes makes it possible to vary their properties making them very promising for use in microelectronics. This generated great interest in research on mesomorphic derivatives of ferrocene, one of the first examples of metal-containing liquid crystals used in studying the structures of the liquid crystal state by Mossbauer spectroscopy. The present work presents results of syntheses and study of certain ferrocene derivatives. A series of liquid crystal ferrocene-containing Schiff bases having the formula $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4-\text{C}_6\text{H}_4-\text{N}=\text{CH}-(\text{X})\text{C}_6\text{H}_3-\text{O}(\text{O})\text{C}-\text{C}_6\text{H}_4-\text{OC}_n\text{H}_{2n+1}$, where $\text{X} = \text{H}, \text{OH}$, and $n = 3-12$ and some of their 1,1'-bis- substituents at the ferrocene group, was synthesized. The analogs have a thermotropic nematic mesophase. Derivatives where $\text{X} = \text{OH}$ yielded chelate complexes of Cu^{2+} and included compounds where $n = 10, 12$ which manifested nematic liquid crystal properties. References 14: 10 Russian, 4 Western.

**Organometallic Synthesis in Furazan Series.
Report 1. Functionalization of
3-Methyl-4-R-Furazans**

927M0194A Moscow IZVESTIYA AKADEMII NAUK
ROSSIYSKOY AKADEMII NAUK SERIYA
KHIMICHESKAYA in Russian No 2, Feb 92
(manuscript received 21 Feb 91) pp 365-371

[Article by A. Yu. Sizov and A. B. Sheremetov, Organic
Synthesis Institute imeni N. D. Zelinskiy, Moscow;
UDC 547.793.2]

[Abstract] Current interest in synthesis of furazan derivatives stems from the fact that some of them have been recommended for application in technology, medicine, and agriculture. As a rule, synthesis of furazans is based on formation of this heterocyclic within a molecule containing the required carbon skeleton by cyclization of corresponding glyoximes. However, the non-availability and relative harsh cyclization conditions of glyoximes limits the number of compounds which may be prepared by this method. Recently, functionally substituted heterocyclics have been successfully synthesized by using metal derivatives. The electron-acceptor characteristics of the furazan ring provide favorable conditions for its metallization; however the literature cites only one example of using this method. In the present work functionally substituted furazans were synthesized from 3-methyl-4-R-furazans by alkylation of their lithium derivatives. In the case of 3,4-dimethylfurazan, both lithium addition and alkylation are possible at either one or both methyl groups. A number of previously unknown furazan derivatives were prepared. References 10: 4 Russian, 4 Western.

**The Problem of the Role of Organometallic
Intermediates in Processes of the
Autohydrogenation of Ethylene, Cyclohexadiene,
and Cyclohexene on Heterogeneous Nickel and
Palladium Catalysts**

927M0197F Moscow KINETIKA I KATALIZ
in Russian Vol 33 No 1, Jan-Feb 92 (manuscript
received 24 Jan 91) pp 121-126

[Article by V.M. Gorelik, I.A. Kopyeva, I.A. Oreshkin,
and B.A. Dolgoplosk, Petrochemical Synthesis Institute
imeni A.V. Topchiyev, USSR Academy of Sciences,
Moscow; UDC 541.128.3:542.941.7:541.124: 547.313:
547.257.4'259.8]

[Abstract] The kinetics of the autohydrogenation of ethylene, cyclohexene, and cyclohexadiene on heterogeneous nickel- and palladium-containing catalysts was

studied. The catalyst for the autohydrogenation of ethylene was produced by impregnating an Ni/silochrome carrier with an aqueous solution of NiCl_2 , drying it in a vacuum, heating it to 350° , and then reducing the salt with a solution of BuLi in hexane. The catalysts for autohydrogenation of cyclohexene and cyclohexadiene were produced by reducing anhydrous NiCl_2 and PdCl_2 with butyl lithium at an Li:M ratio of 1:10. The Pd/ Al_2O_3 catalyst was produced by impregnating $\gamma\text{-Al}_2\text{O}_3$ with a solution of PdCl_2 in concentrated HCl, drying the mixture at 120° , impregnating it with an allyl alcohol solution, and heating it for 3 hours at 200° . The autohydrogenation reactions were all conducted in ampules, and all of the mixtures were subjected to chromatographic analysis. The studies performed established that in the case of autohydrogenation of ethylene on an Ni^0 /silochrome catalyst, limiting values of the ethane yield over time (G_a) amounted to 0.15-0.2, 0.3, and 0.6-0.7 mol/mol Ni at temperatures of 22, 70, and 150° , respectively. Hydrolysis of the catalyst after the end of the reaction after the gaseous products in the vacuum had been removed was found to result in the evolution of an additional amount of ethane. When the autohydrogenation was conducted at 22° , the amount of ethane evolved upon subsequent hydrolysis of the catalyst (G_b) reached 1.5 moles per mole of ethane formed during the course of the autohydrogenation (0.25 mol/mol Ni) in the initial stage of the reaction and then decreased somewhat to about 0.7 mol/mol ethane evolved during autohydrogenation (0.15 mol/mol Ni). When the autohydrogenation was conducted at 150° , the yield of ethane after hydrolysis decreased to 0.02-0.05 mol/mol Ni. These findings led the researchers to hypothesize that some amount of stable $-\text{Ni}-\text{C}_2\text{H}_5$ fragments whose hydrolysis results in ethane formation is preserved on the surface during the course of the autohydrogenation reaction. The proximity of G_a and G_b was taken as confirmation of the fact that at 22° , the autohydrogenation reaction occurs stoichiometrically with respect to the active metal. The noncatalytic nature of the reaction was evidently linked to inhibition in the carbide formation stage. Further studies established that CO and CO_2 have an inhibiting effect in the processes studied. Studies of the autohydrogenation of cyclohexadiene and cyclohexene with catalytic systems based on Ni^0 and Pd^0 established that the reaction results in the formation of equimolar quantities of cyclohexene and benzene. Analogous results were obtained when an $\text{Ni}^0/\text{NiCl}_2$ catalyst system was used. The cyclohexene formed under the said conditions did not undergo further transformation. The autohydrogenation of cyclohexadiene on Pd/ PdCl_2 was observed to occur more deeply with the formation of benzene and cyclohexane in a 2:1 molar ratio. The cyclohexene formed during the reaction was determined to be an intermediate product. Figures 6, table 1; references 12: 5 Russian, 7 Western.

Asymmetric Synthesis of Elementorganic Analogs of Natural Compounds. Report 6. (S)- α -Amino- ω -phosphonocarboxylic Acid

927M0194B Moscow IZVESTIYA AKADEMII NAUK
ROSSIYSKOY AKADEMII NAUK SERIYA
KHIMICHESKAYA in Russian No 2, Feb 92
(manuscript received 20 Feb 91) pp 397-402

[Article by V. A. Soloshonok, N. Yu. Svistunova, V. P. Kuzhar, V. A. Solodenko, N. A. Kurmina, A. B. Rozhenko, S. V. Galushko, I. P. Shishkina, A. O. Gudima, and Yu. N. Belokon, Elementorganic Compounds Institute, Moscow; UDC 542.91:547.466.416]

[Abstract] Both natural and synthetic phosphorus analogs of amino acids are biologically active. Amongst the dicarboxylic amino acid analogs, phosphinotricin has attracted the most attention. This compound has high antibacterial and herbicidal activity, while α -amino- ω -phosphonocarboxylic acid is an effective and selective antagonist stimulating amino acids. In the present work the Ni(II)-complex of Schiff glycine with (S)- 2N-(N¹-benzylpropyl)-o-aminobenzophenone was alkylated with ω -halogonalkylphosphonates to prepare the title acids. Figure 1; references 25: 5 Russian, 6 Western.

**Extraction Separation and Chromatographic
Determination of Some Chloro- and
Phosphorus-Organic Pesticides in Three Phase
Systems**

927M0236D Moscow *ZHURNAL ANALITICHESKOY
KHIMII in Russian* Vol 47 No 6, Jun 92 (manuscript
received 26 Apr 91) pp 1058-1065

[Article by V. A. Frankovskiy, V. I. Kofanov, Yu. V. Lushnikova, Kiev State University imeni T. H. Shevchenko; Institute of Colloidal Chemistry and Chemistry of Water imeni A. V. Dumanskiy, Ukrainian Academy of Sciences, Kiev; UDC 542.61:547:551]

[Abstract] Extraction procedures for sixteen pesticides were investigated using a three phase extraction system

consisting of hexane and a polar organic phase consisting of acetonitrile, methanol, nitromethane, dimethylacetamide and dimethylformamide in presence of aqueous potassium carbonate. As a preliminary step, extraction in two phase system (without aqueous potassium carbonate) could be used to remove co-extracted substances from the pesticides extracts. The three phase system consisting of 36-44% aqueous potassium carbonate solution, methanol, dimethylacetamide or dimethylformamide and hexane was recommended for quantitative separation of chloro-organic and phosphorus-organic pesticides. The distribution coefficients were determined for both the two and three phase systems and factors were determined affecting them and correlated with the polarity of the solvents and pesticide molecules. Tables 7; figure 1; references 8: 6 Russian, 2 Western.

Characteristics of Porous Structure Development During Carbonization of Crushed and Granulated Low Grade Coal

927M0235C St. Petersburg ZHURNAL PRIKLADNOY KHIMII in Russian Vol 65 No 1, Jan 92 (manuscript received 10 Jan 91) pp 108-112

[Article by Yu. A. Romanov, N. V. Limonov, G. K. Ivakhnyuk, Technological Institute, St. Petersburg; UDC 661.183]

[Abstract] An attempt was made to find a relationship between the mass yield, the volume change in the starting coal and the carbonization temperature. In addition, the characteristics of the development of specific pores were studied in crushed and granulated low grade coal. It was shown that in the low temperature phase of the carbonization process, the principal process was the formation of macroporous structures. In case of granular material, this was the result of the removal of the binder pyrolysis products and of the volatile material up to the temperature of 620 K; along with it the formation of transport porosity volumes resulting from packing of the coal particles took place. In case of crushed coal, the distribution of organic mass and removal of the volatile substances predetermined the formation of transport pores characterized by polymodal distribution according to their size. In the high temperature stage of carbonization the above processes were the same for the crushed and granulated coal: topochemical conversion of coal particles, marked grain settling accompanied by formation of considerable volume of micropores with preservation

of the earlier formed transport pores. Tables 3; figures 2; references 9: 7 Russian, 2 Western.

Isolation of Sulfur and Microelements From Highly Viscous Petroleum and Petroleum Bitumen Rocks

927M0235F St. Petersburg ZHURNAL PRIKLADNOY KHIMII in Russian Vol 65 No 1, Jan 92 (manuscript received 10 Apr) pp 201-206

[Article by N. K. Nadirov, L. V. Bychkova, N. V. Rudenko, A. N. Dzhakupova, B. K. Sarsembayeva, Scientific Production Association "Kazneftebitum"; UDC 665.61.033.55]

[Abstract] The oil from Western Kazakhstan shows heterogeneous chemical composition; some of the components could be used in many industrial applications. Ultrasound and ionizing radiation could be used to process these crudes, lowering the energy consumption, extending the performance of equipment and lowering the emission of toxic substances into the atmosphere. Specifically, these operations could help in selective removal of sulfurous concentrate and various microelements. Radiation-chemical concentration diminishes losses of microelements; ultrasound accelerates the process and phase separation. Individual metals can be isolated with selective solid extracting agents. The effectiveness of these isolation processes depends on the irradiation dose, the processing conditions (pH and temperature), the solid extraction agent and on the condition of acid breakdown. Tables 2; figures 2; references: 17 (Russian).

Silylation in Polymer Chemistry

927M0234C Moscow USPEKHI KHIMII in Russian
Vol 61 No 6, Jun 92 pp 1142-1180

[Article by R. D. Katsarava, Ya. S. Vygodskiy, Institute of Molecular Biology and Biophysics, Georgian Academy of Sciences, Institute of Metal Organic Compounds imeni A. N. Nesmeyanov, Russian Academy of Sciences; UDC 541.64]

[Abstract] Replacement of an active hydrogen atom in many organic compounds by a tris(hydrocarbonyl)-silyl or trimethylsilyl group makes it possible to solve a number of synthetic problems: peptide synthesis, protection of amino, carbonyl or hydroxy groups, separation of aminoacids by chromatography, etc. In this review the authors attempted to summarize existing data and to supplement them with new findings, especially in the area of polymer condensation, polymerization and polymer chain reactions. The subtopics of this review extend to: synthesis of silylated monomers and their properties; synthesis of polymers from monomers with N-Si bonds (polyamines, polyazomethines, polythiazines, polyamides, polyurethanes, polyureas and polycycloimides), synthesis of non-cyclic linear polyimides and of photosensitive polymers. Next section covered polymers based on compounds with a O(S)-Si bond, followed by sections on polycondensation in situ, polymerization of heterocycles, polymerization of silyl enol ethers and finally reactions in polymer chains. In spite of the multitude of publications in this field, so far it still has not been possible to scale up this method to the industrial level. References 165: 49 Russian (1 by Western author), 116 Western (5 by Russian authors).

Sorption of Palladium (II) From Hydrochloric Acid Solutions on Polymer Impregnated With Sulfoxides

927M0235D St. Petersburg ZHURNAL PRIKLADNOY KHIMII in Russian Vol 65 No 1, Jan 92 (manuscript received 5 Jul 91) pp 121-125

[Article by A. N. Turanov, Institute of Physics and Solid Bodies, Russian Academy of Sciences; UDC 542.61:546.982]

[Abstract] The distribution time of palladium (II) between hydrochloric acid solution and a macroporous styrene copolymer with divinylbenzene impregnated with didodecyl sulfoxide or a mixture of paraffine sulfoxides or sulfoxide solution of o-xylene in presence of tributylphosphate (TBP) was investigated. In case of didodecyl sulfoxide, the equilibrium of Pd(II) extraction was reached very slowly; the process accelerated somewhat with increasing concentration of HCl. The extraction process was markedly accelerated with addition of TBP to the organic phase. Overall, it was shown that the impregnated macroporous copolymer of styrene and divinylbenzene absorbed effectively Pd(II) in a wide range of HCl concentrations. It is a much faster process than liquid extraction. Table 1; figures 4; references 8: 7 Russian, 1 Western.

Use of Copper-Selective Electrode in Determination and Investigation of Monomer and Polymer Amino Sugars

927M0236E Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 47 No 6, Jun 92 (manuscript received 13 Mar 91) pp 1076-1082

[Article by S. L. Davydova, L. V. Chervina, Institute of Petrochemical Synthesis imeni A. V. Topchiyev, Russian Academy of Sciences, Moscow; UDC 543.257.1:547.455.6]

[Abstract] This is one of a series of papers presented at the All Union Conference on Analytical Chemistry of Organic Compounds held in Moscow, 23-25 June 1991. The possibility of using copper selective membrane electrode (Cu-SE) in determining derivatives of D-2-glucose amine was investigated. The effect of various factors on the accuracy of this method was studied: pH, the nature of buffer solution, preparatory procedures, etc. On the basis of experimental data obtained, a titration method for micro detection of monomer and polymer amino sugars was developed for materials with varying molecular weights and solubility. The procedure is based on complexing the NH₂-groups of the studied sugars with copper (II) in a basic medium, controlling the reaction with potentiometric titration using Cu-SE indicator. The sensitivity of this method is 1-50 mg of amino sugars and the experimental error is 0.5-1 rel-%. Table 1; figures 2; references 10: 6 Russian, 4 Western.

Catalytic Oxidation of Wood and Its Components Under Conditions of Oxidizing Delignification Methods. 1. The Effect of Potassium Ferricyanide on the Oxidation Rate of Wood and Its Components

927M0198A Riga KHIMIYA DREVESINY in Russian No 5, Sep-Oct 91 (manuscript received 10 Dec 90; after revision 22 May 91) pp 19-25

[Article by E.I. Chupka, S.Zh. Trofimova, S.V. Yegorova, and I.M. Luzhanskaya, All-Union Paper and Pulp Industry Scientific Production Association; UDC 634.0.861.16]

[Abstract] It has been proposed that the use of specific catalysts for selective conversion of molecular oxygen into a stronger oxidizing agent, i.e., into a hydroxyl radical, may be an effective way of improving oxidation-based delignification methods. The effect of the concentration of $K_3Fe(CN)_6$ on the rate of OH and O_2^- generation and on the oxidation of wood, lignin, and carbohydrates was studied. The rate of oxygen consumption during the oxidation of aspen wood was determined by the micromanometric method. Oxygen consumption as a function of the $K_3Fe(CN)_6$ concentration reached a maximum at a $K_3Fe(CN)_6$ concentration of 6×10^{-2} mol/l. At that point, the rate of oxygen consumption amounted to 5.0×10^{-10} mol/(l x c), which is fourfold the rate achieved in control specimens without the addition of $K_3Fe(CN)_6$. The rate of OH formation increased as the $K_3Fe(CN)_6$ concentration increased. At a $K_3Fe(CN)_6$ concentration of 0.4 mol/l, the rate of OH formation increased by threefold vs. the rate found in the control experiments. The micromanometric studies performed also established that the rate of OH generation during glucose oxidation remains virtually unchanged. Thus, during the oxidation of arabinogalactan, there is a sharp increase in the rate of OH generation while the rate of overall oxidation decreases. The use of $K_3Fe(CN)_6$ as a catalyst thus made it possible to regulate the ratio of stationary concentrations of active forms of oxygen with very different oxidation properties and to combine the cellulose production process with continuous synthesis of peroxide during the oxidation of both wood and its components. Figures 10; references 15: 13 Russian, 2 Western.

Amino Lignin Derivatives. 2. Desoxyamination Through Tosyl Esters

927M0198B Riga KHIMIYA DREVESINY in Russian No 5, Sep-Oct 91 (manuscript received 26 Feb 91) pp 54-60

[Article by G.F. Zakis and B.Ya. Neybert, Wood Chemistry Institute, Latvia Academy of Sciences; UDC 547.992.3:542.958.3]

[Abstract] Gabriel's reaction is one important way of introducing primary amino groups into hydroxyl-containing compounds. The possibility of synthesizing lignin via tosyl esters was investigated. The starting lignin tosylate was produced in accordance with Friedenberg's method from Willstater's spruce lignin. The tosylate and potassium phthalimide were condensed in a dimethyl formamide medium. The synthesis process temperature was varied from 20 to 153°C, and the process duration was varied from 1 to 10 hours. The product obtained from a regimen of condensation in boiling dimethyl formamide (153°C for 6 hours) contained 3.91% nitrogen and 7.59% OCH_3 . The product consisted primarily of a mixture of phthalimide and partially detosylated tosylate. Gabriel's reaction was found to proceed anomalously with lignin tosylate and to thus be without promise as an amination method. The route of nucleophilic substitution of tosylates by amines was tried as an alternative desoxyamination method. All of the amines tested yielded nitrogen-containing amino derivatives. For all practical purposes, the reaction was over in half an hour. All of the reaction products still contained sulfur (3.64 to 4.53%). Next, tosylate was reacted with n- and sec-butylamine, monoethanolamine, benzylamine, diethylamine, and piperidine for 2 hours at 120°C. Amino lignin derivatives were produced that contained from 2.1 to 9.1% nitrogen, which is equivalent to adding 0.42 to 0.64 amino groups per phenyl structural unit. Primary amines were found to be more reactive than secondary ones. The amino derivatives produced were found to be polybases with an exchange capacity of 1.90 to 3.19 mEq/g. Figures 2, tables 4; references 13: 8 Russian, 5 Western.

Some Principles of Teaching Coordination Chemistry

827M0180B Moscow KOORDINATSIONNAYA KHIMIYA in Russian Vol 18, No 1, Jan 92 (manuscript received 21 May 91) pp 26-33

[Article by B. D. Berezin, Institute of Chemistry of Non-aqueous Solutions AS USSR; UDC 541.49]

[Abstract] The article described some principles of teaching coordination chemistry emphasizing discussion of the concepts: complex formation, complex compound, coordination compound, coordination number and other concepts. It described similarities and differences between the concepts "complex compound" and "coordination compound" and "chemistry of complex compounds" and "coordination chemistry". References 15 (Russian).

A New Type of Gold-Silver Deposits in Northeastern Russia

927M0184A Moscow SOVETSKAYA GEOLOGIYA in Russian No 4, Apr 92 (manuscript received 29 Oct 90) pp 17-26

[Article by I.S. Rozenblyum, Sevvostgeologiya Polar Geophysical Observatory, A.I. Kalinin, Northeastern Affiliate, Central Scientific Research Institute for the Mining and Prospecting of Nonferrous, Rare, and Noble Metals, V.N. Makurin, L.M. Yarantseva, and M.V. Boldyrev, Sevvostgeologiya Polar Geophysical Observatory; UDC 553.41(571.65)]

[Abstract] Until recently, the only known volcanogenic gold-and-silver mineralization of commercial scale within the confines of northeastern Russia was linked to the volcanic-igneous associates of the Okhotsk-Chukot belt. In the past few years, however, it has been discovered that similar mineralization also occurred in the structures of the Omolon central rock mass under very different geotectonic circumstances. A study of a standard deposit in the southern part of the Omolon rock mass (the South Omolon ore region) confirmed that the Omolon deposits represent a new type of gold-and-silver mineralization that is indeed very different from the typical deposits of the Okhotsk-Chukot volcanogenic belt. The main distinctions of the Omolon rock mass are 1) its specific position in regional structures dictated by the effect of deep meridional faults and 2) the duration and complexity of ore field's geological history as reflected in the special characteristics of its deep structure, the structure of the deposit, the morphology of the ore bodies present, their composition, and the laws governing distribution of the mineralization. The foundation of the Omolon rock mass is a series of Archean formations with a total thickness of about 20 km. The cover is made up of sedimentary and sedimentary-volcanic masses that form three tiers. The bottom tier consists of Sinian and Ordovician terrigenous and carbonate sediments with a total thickness of up to 3,500 m along with Lower Paleozoic intrusive complexes. The middle tier consists of subaerial volcanic rock of the Devonian period along with marine and shore volcanogenic-sedimentary

deposits and igneous rocks dating from the Middle Devonian period. The upper tier consists of terrigenous, terrigenous-carbonate, and volcanogenic formations of the Late Devonian-Late Jurassic period with a total thickness of 200 to 6,000 m. The most significant special features of the geodynamic position of the mineralization in the Omolon rock mass are 1) its belonging to the long-lived meridional shear zone of tectonic-magmatic activation and 2) the extensive development of shore faults that are kinematically linked to it and that together with it reflect a stage of big horizontal displacements. The Avlandinskiy ore node is distinguished by its heterogeneity: It contains gold-and-silver, gold-and-rare metal, and gold-and-sulfide ore deposits along with ferrous quartzite and magnetite scars and copper-molybdenum-porphyry formations. Overall, the ore deposit represents a very inhomogeneous body of individual ore deposits with greatly contrasting physico-mechanical properties and a very diverse chemism. The central, northern, and foundation vein zones of the southern Omolon region are the most interesting in that they contain commercial ore bodies. At least 40 minerals are present, including round agglomerates of gold up to 3 mm in diameter. The main form in which the gold and silver are present in the deposit are 1) as native gold and 2) in minerals of the gold-silver series (electrum, kustelite, native silver). Analysis has established the existence of two generations of native gold and silver phases. The overall distribution of mineralization in the Omolon rock mass is highly uneven. Figures 5, tables 2; references 5 (Russian).

Au-Element Bond Lengths and Nature of Trans-Effect in Mono-Valent Gold Complexes

927M0233A Moscow METALLOORGANICHESKAYA KHIMIYA in Russian Vol 5 No 4 Jul-Aug 92 (manuscript received 25 Oct 91) pp 744-781

[Article by L. G. Kuzmina, Institute of General and Inorganic Chemistry imeni N. S. Kurnakov, Russian Academy of Sciences, Moscow; UDC 548.737]

[Abstract] This article represents a review of literature data analyzing in detail various mono-valent gold complexes. Bond length of gold-element linear complexes were analyzed. The Au-O bonds range from 2.02 to 2.06 Angstrom in complexes with phenols as well as with inorganic acids. The Au-N bonds are stretching over 1.88-2.18 Angstrom. The Au-S length is narrower: 2.24-2.34 Angstrom and Au-C bond length depends on the carbon atom hybridization state. In case of Au-P complexes the bond length depends on the QX ligand in trans position to the phosphorus ligand; its length parallels the increase of the σ -donor potential of the QX ligand. The material presented should be of interest to chemists and crystallographers by identifying many new structural effects such as the contribution of the resonance component or the trans-effect in these complexes. Tables 7; figures 5; references 199: 30 Russian (1 by Western author), 169 Western (10 by Russian authors).

Crystalline Phosphor for Luminescent Storage Screens

927M0234A Moscow USPEKHI KHIMII in Russian
Vol 61 No 6, Jun 92 pp 1047-1060

[Article by A. M. Gurvich, V. V. Mikhaylin, Moscow Scientific X-ray-Radiological Research Institute, Moscow State University; UDC 541.1;535.37;535.376]

[Abstract] A review of papers covering photostimulating crystalline phosphors for luminescent storage screens used in digital radiography has been presented. The survey covered seven sub-topics: storage luminescent screens as an alternative to silver halide photographic materials; selection of crystalline phosphors for storage screens; structure and basic properties of barium fluoro halides; BaFBr:Eu-phosphor properties as a function of preparatory conditions; BaFBr:Eu-phosphor crystalline lattice defects and the mechanism of photostimulating luminescence; excitation spectra of stationary luminescence, phosphorescence and photostimulating luminescence of barium fluoro halides; some applications of luminescent storage screens. Development of effective crystalline phosphors for luminescent storage screens based on their application created a new field of research actively pursued in many directions. Figures 4; references 94: 19 Russian, 75 Western (10 by Russian authors).

Silicon Subgroup Elements Conjugation in Organic Compounds

927M0234B Moscow USPEKHI KHIMII in Russian
Vol 61 No 6, Jun 92 pp 1092-1113

[Article by A. N. Yegorochkin, Institute of Metal Organic Chemistry, Russian Academy of Sciences, Nizhny Novgorod; UDC 541.65:547.1'3]

[Abstract] The goal of this review was to analyze the existing theoretical and experimental material on intramolecular reactions and on the effects of conjugation in silicon subgroup compounds. The review was prepared by first selecting the general theoretical concept: the most exhaustive compilation of experimental data on intramolecular reactions and, on its basis, identification of weak points in literature. This was followed by comparison of this concept with alternative approaches to explain the experimental factors and finally, determination of the applicability of the selected concept. The principal attention was paid to: 1) studies important to the development of the topic, and 2) the most studied compounds of tetracoordinated elements of silicon subgroups. It was shown that the resonance effect of element-organic substituents includes the acceptor component (concurrent effect of vacant nd- and loose anti-bonding σ^* orbitals) and a donor component (σ, π , σ, π^* - and σ, n - conjugation). Relative contribution of these components to the resonance effect was analyzed as a function of the central element, organic groups connected with it and the reactive center. Figures 2; references 161: 51 Russian (4 by Western authors), 110 Western (7 by Russian authors).

Synthesis and Investigation of Diamond-Oxide Systems Based on Ultradispersed Diamonds

927M0235B St. Petersburg ZHURNAL PRIKLADNOY KHIMII in Russian Vol 65 No 1, Jan 92 (manuscript received 4 Apr 91) pp 34-47

[Article by T. M. Gubarevich, A. V. Tyshetskaya, Scientific Production Association "Altay"; UDC 666.233]

[Abstract] Diamonds possess a number of unique properties: high thermal conductivity, high specific electric resistance, chemical, mechanical and radiation stability. They are used in production of electronic equipment components. Ultradispersed diamonds represent rather novel synthetic materials. In the present work diamond particles were combined with Ni, Mg, Cu, B and Al oxides. The diamond-oxide systems were prepared by thermal decomposition of respective nitrates or acids in presence of ultradispersed diamonds; the products contained 30 to 95% of the diamond. Depending on the composition, the diamond-oxide systems exhibit different properties: Ni and Mg oxides facilitate oxidation of ultradispersed diamonds, Al and B oxides increase their thermal stability. EM and x-ray phase analysis of the diamond-oxide samples showed that their properties differed from mechanical mixtures of similar composition. Table 1; figures 4; references: 5 (Russian).

Amperometric Immuno-enzymatic Electrode Based on Immobilized Cholinesterase

927M0236F Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 47 No 6, Jun 92 (manuscript received 13 Mar 91) pp 1101-1106

[Article by E. P. Medyantseva, S. S. Babkina, G. K. Budnikov, I. L. Fedorova, N. N. Ibragimova, Kazan State University; UDC 543.253:577.087.4:546/7]

[Abstract] This is one of a series of papers presented at the All Union Conference on Analytical Chemistry of Organic Compounds held in Moscow, 23-25 June 1991. The goal of this work was to develop new immuno-enzymatic electrodes (IEE) which could be used in heterogeneous immuno-enzymatic analysis without preliminary separation of the components of the test sample. The sensor of this newly developed IEE included immobilized cholinesterase and a biological component (an antigen or antibody). It was used in diagnosis of Aleutian disease of minks, a slow viral infection which results in poor fur quality in the affected animals. Present diagnostic methods are very time consuming and difficult. This new method provides accurate diagnosis (verified by classical radio-immuno assay) in 15 min rather than several hours normally needed. The sensitivity of this assay is 10^{-10} mol/l. Table 1; figures 3; references 14: 12 Russian (1 by Western author), 2 Western.